

α -(Acetyl-D-amino)butyric Acid Monohydrate

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Abstract. $C_6H_{11}NO_3 \cdot H_2O$, $M_r = 163.17$, orthorhombic, $P2_12_12_1$, $a = 5.835$ (4), $b = 7.756$ (3), $c = 19.910$ (7) Å, $Z = 4$, $D_x = 1.090$ Mg m⁻³. The structure was solved by direct methods and refined to an R value of 0.045 for the 886 reflexions. The amide bond is in the *trans* conformation. The peptide occurs in conformation F^* , with $\varphi = 74^\circ$ and $\psi = -158^\circ$. An extensive network of intermolecular hydrogen bonds holds the crystal together in the solid state.

Introduction. α -(Acetyl-D-amino)butyric acid (Ac-D-Abu-OH) was obtained as a crystal among other crystals obtained from the slow evaporation of an aqueous solution of the commercially available α -L-aminobutyric acid (Fluka, Buchs). The preparation of the latter, achieved through acylation of the racemic amino acid mixture and subsequent enzymatic resolution, also leaves α -(acetyl-D-amino)butyric acid (Marshall, Birnbaum & Greenstein, 1956) as impurity. Intensity data were collected with the Enraf-Nonius CAD-4 SDP 11/34 diffractometer of the Centro di Metodologie Chimico-Fisiche of the University of Naples, using the ω - 2θ scan mode with Cu $K\alpha$ radiation and a range of $(1.00 + 0.15 \tan \theta)^\circ$ for the peak measurements. Background counts were taken at each end of each scan. Reflections with a net intensity $I \leq 0.5\sigma(I)$ were flagged as 'weak'; those having $I > 0.5\sigma(I)$ were measured at a slower speed (in the range $1-4^\circ \text{ min}^{-1}$) depending on the value of $\sigma(I)/I$. A total of 1043 reflections were collected; of these, 886 had a net intensity greater than $3\sigma(I)$. All reflections were corrected for Lorentz and polarization factors; no absorption correction was applied. The structure was solved by direct methods using the program *MULTAN* (Germain, Main & Woolfson, 1971) included in the SDP package. The structure was then refined using a least-squares procedure to a final R value of 0.045 with anisotropic temperature factors for C, N and O atoms, and isotropic temperature factors for H atoms. The positions of the H atoms were determined from a difference Fourier map, except for those linked to C^β and C^γ , which were fixed in their stereochemically expected positions. The H atoms of the water molecule were found to be statistically distributed over two

positions which were, eventually, both refined. The H atom of the carboxyl group was not located, perhaps because of the statistical disorder present in this group. A weight $w = 1/\sigma^2(F_o)$ was employed. Atomic scattering factors were taken from Cromer & Waber

Table 1. Positional parameters ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{Å}^2 \times 10^3$) for the non-hydrogen atoms

	x	y	z	U_{eq}^*
C_0^o	5470 (8)	3461 (6)	842 (2)	57 (3)
C_0^i	3226 (7)	2716 (5)	1064 (2)	42 (2)
O_0	1368 (5)	3395 (4)	932 (1)	56 (2)
N	3294 (5)	1239 (4)	1420 (1)	37 (3)
C^α	1198 (6)	449 (5)	1663 (2)	38 (3)
C^β	1687 (8)	-838 (6)	2230 (2)	58 (4)
C^γ	2969 (9)	-2433 (7)	2021 (3)	77 (5)
C'	-179 (6)	-415 (4)	1100 (2)	35 (3)
O	806 (4)	-876 (3)	576 (1)	42 (3)
O_7	-2265 (4)	-617 (4)	1216 (1)	48 (2)
OW	5218 (5)	-895 (4)	26 (2)	60 (3)

$$* U_{eq} = (U_{11} U_{22} U_{33})^{1/3}.$$

Table 2. Positional and thermal parameters for hydrogen atoms

$$T = \exp(-B \sin^2 \theta / \lambda^2); \text{ fractional coordinates are } \times 10^3.$$

	x	y	z	B (Å ²)
$H1C_0^\alpha$	322 (8)	-212 (6)	400 (2)	5 (1)
$H2C_0^\alpha$	448 (10)	-144 (7)	466 (2)	7 (2)
$H3C_0^\alpha$	435 (9)	-44 (7)	397 (2)	8 (1)
HN	447 (8)	78 (5)	152 (2)	5 (1)
HC^α	16 (9)	148 (7)	187 (2)	3 (2)
$H1C^\beta$	6	-128	246	5
$H2C^\beta$	268	-24	263	5
$H1C^\gamma$	323	-327	243	6
$H2C^\gamma$	196	-306	163	6
$H3C^\gamma$	458	-201	181	6
$H1OW$	659 (12)	-86 (8)	45 (3)	2 (1)
$H2OW$	346 (12)	-70 (9)	18 (3)	2 (2)
$H3OW$	589 (12)	8 (9)	-37 (3)	2 (2)
$H4OW$	537 (13)	-222 (9)	-24 (3)	2 (2)

(1974). The final atomic parameters are listed in Tables 1 and 2.*

Discussion. The molecular model of Ac-D-Abu-OH with bond lengths and bond angles is shown in Fig. 1. The values are unexceptional and agree well with the standard values for peptides. The e.s.d.'s for the bond distances and angles are 0.007 Å and 0.5° respectively. The conformation of the molecule is described by the torsion angles given in Table 3,† in which the conformations of the Abu residue in structures of cyclosporin A (Petcher, Weber & Ruegger, 1976), factor S of virginiamycin (Declercq, Germain, Van Meerssche, Hull & Irwin, 1978) and DL-Abu-OH (Ichikawa & Iitaka, 1968) are also given for comparison. The peptide bond is found in the *trans*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35780 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† The abbreviation, the description of the atoms, and the convention for the conformation of the polypeptide chain follow the recommendations of the IUPAC-IUB Commission on Biochemical Nomenclature (1970).

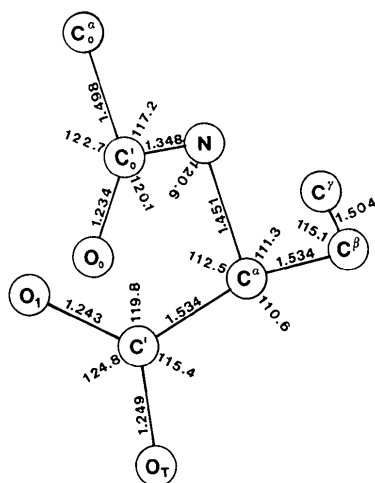


Fig. 1. Molecular model of Ac-D-Abu-OH with its geometry.

conformation ($\omega = 179^\circ$). The ϕ and ψ values in Ac-D-Abu-OH fall in the ' β -structure region' of Ramachandran's plot (Ramachandran, Ramakrishnan & Sasisekharan, 1963). According to the notation introduced by Zimmerman, Pottle, Nemethy & Scheraga (1977) the peptide occurs in the conformation F^* . The χ^1 angles, defining the orientation of the side chain, for the various Abu residues may be classified into three groups with values of approximately -60 , 180 and $+60^\circ$, all of which have been found experimentally in the crystal structures reported in Table 3.

The six atoms of the amide group, including the H atom linked to the N, lie in a plane with deviations from the best plane not greater than 0.008 Å. The dihedral angle between the *N*-acyl and the carboxyl group is 97° , in agreement with those observed in other *N*-acyl amino acids and peptides (Chen & Parthasarathy, 1978).

As reported in Fig. 2, the packing is governed by the formation of hydrogen bonds involving the water molecule and all the possible acceptors and donors of H bonds of the peptide molecule. In the *ab* plane two sheets of symmetry-related molecules face each other and are linked through water molecules by H bonds: the polar portion of each sheet faces that of the

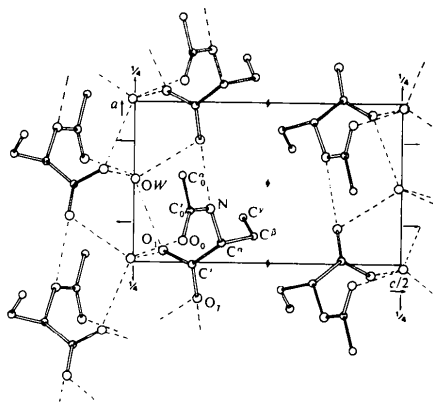


Fig. 2. Mode of packing of Ac-D-Abu-OH as viewed along the *b* axis. Hydrogen bonds are indicated by dashed lines.

Table 3. Torsion angles ($^\circ$) in crystal structures containing the Abu moiety

Compound	ω	ϕ	ψ	χ	References
Acetyl-D-Abu-OH	179	74	-158^*	-68	This work (average e.s.d. 2°)
Cyclosporin A	178	-146	124^*	174	Petcher <i>et al.</i> (1976)
Factor S of virginiamycin	-179	-105	-111^*	-60	Declercq <i>et al.</i> (1978)
DL-Abu-OH (monoclinic)	—	—	163^*	-175^\dagger	Ichikawa & Iitaka (1968)
				73	
				-54	
DL-Abu-OH (tetragonal)	—	—	151^*	-176	Ichikawa & Iitaka (1968)

* These values refer to the torsion angle $N-C^\alpha-C'-O_T$ in which O_T is the oxygen atom of the carboxyl group *trans* to the N atom.

† The three values pertain to the statistical model proposed for the side chain of the molecules in the crystalline state.

symmetry-related sheet (through the operation of the screw axes contained in the *ab* plane), the water molecules being the 'cement' that holds together the resulting double layer. Such bilayers pack with each other through hydrophobic interaction in the *c* direction. The formation of these bilayers resembles that found in the crystal structure of amino acids.

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Dimethyl 3-(1-Pyrrolidiny)benzo[*b*]thiocin-4,5-dicarboxylate

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Abstract. $C_{19}H_{21}NO_4S$, $M_r = 359.1$, triclinic, $P\bar{1}$, $a = 9.919$ (4), $b = 10.518$ (5), $c = 10.240$ (5) Å, $\alpha = 93.32$ (4), $\beta = 95.99$ (4), $\gamma = 58.43$ (3)°, $V = 905.2$ Å³, $Z = 2$, $D_c = 1.32$ Mg m⁻³; $R = 0.046$ for 1520 diffractometer data. The structure contains a new type of thiocin ring, which has a rigid boat conformation.

Introduction. The compound was prepared and crystallized by Lamm & Aurell (1980). It was obtained through a (2 + 2) cycloaddition of dimethyl acetylenedicarboxylate to the pyrrolidine enamine of thiochroman-3-one, followed by acid-catalysed ring opening. Yellow crystals were grown from an ether solution. The crystal used for data collection was a parallelepiped 0.16 × 0.10 × 0.12 mm. Cell parameters and intensities were obtained on a four-circle automatic Syntex P2₁ diffractometer with the θ –2 θ scan method and graphite-monochromatized Mo $K\alpha$ radiation. 2016 reflections were collected up to $2\theta = 42^\circ$. The 2θ scan speed was varied between 3 and 30° min⁻¹ and a 96-step profile was recorded for each reflection. The profile analysis was made according to the Lehmann & Larsen (1974) method with LELA (Lindqvist & Ljungström, 1979). The intensities were corrected for Lorentz and polarization effects, but not for absorption.

The crystal structure was solved with MULTAN 77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977). The complete non-hydrogen skeleton was found and the refinement of these atoms with isotropic temperature factors by the least-squares block-diagonal approximation gave $R = (\sum |F_o| - |F_c|) / \sum |F_o| = 0.11$. H atoms were located from a difference map. The final refinement ($R = 0.046$) was based on 1520 observed reflections having $I > 3\sigma(I)$, and included isotropic and anisotropic thermal parameters for the H and non-hydrogen atoms, respectively. The weights were calculated as $w = 1/(A + F_o + CF_o^2)$ with $A = 35.0$ and $C = 0.0025$ giving a good weight analysis.

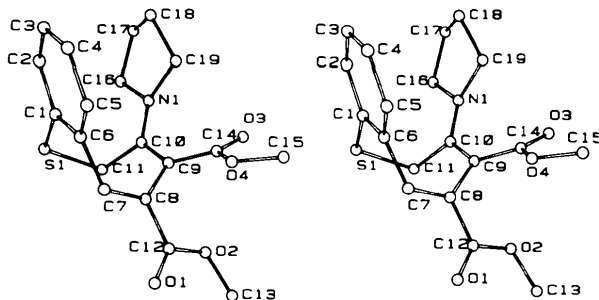


Fig. 1. Stereoscopic picture of the molecule (ORTEP; Johnson, 1965). The notation is in accordance with Tables 1–3.