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Structures of *N*-Acetyl-α-aminoisobutyric Acid, $C_6H_{11}NO_3$, and *N*-Trifluoroacetyl-α-aminoisobutyric Acid, $C_6H_8F_3NO_3$*

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Abstract. $C_6H_{11}NO_3$ (Ac-Aib-OH; Ac, acetyl and Aib, α-aminoisobutyric acid): $M_r = 145{\cdot}16$, monoclinic, $P2_1/n$, $a = 10{\cdot}165\,(4)$, $b = 8{\cdot}030\,(4)$, $c = 9{\cdot}712\,(4)$ Å, $\beta = 111{\cdot}9\,(3)°$, $V = 736\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}31$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}98$ cm^{-1}, $F(000) = 312$, $T = 295$ K. $C_6H_8F_3NO_3$ (F_3Ac-Aib-OH; F_3Ac, trifluoroacetyl): $M_r = 199{\cdot}13$, orthorhombic, *Pcab*, $a = 15{\cdot}174\,(5)$, $b = 11{\cdot}773\,(4)$, $c = 10{\cdot}092\,(4)$ Å, $V = 1803\,(1)$ Å^3, $Z = 8$, $D_x = 1{\cdot}467$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}46$ cm^{-1}, $F(000) = 816$, $T = 295$ K. Final *R* values 0·042 for 1053 independent observed reflections for Ac-Aib-OH and 0·085 for 1121 independent observed reflections for F_3Ac-Aib-OH. In both compounds the conformation of the amide bond is *trans* and the Aib residue shows a φ, ψ_T set of torsion angles falling in the region of the Ramachandran map where α- and 3_{10}-helices are found. The dihedral angle δ between the amide and carboxylic acid groups is 101·1 (3) and 73·0 (6)° for Ac-Aib-OH and F_3Ac-Aib-OH respectively.

Introduction. As a part of our continuing study on the preferred conformations of the α,α-dimethylated α-amino acid Aib (Toniolo, Bonora, Bavoso, Benedetti, Di Blasio, Pavone & Pedone, 1983; Valle, Bonora & Toniolo, 1984) we describe here the results of an X-ray diffraction analysis of Ac-Aib-OH and F_3Ac-Aib-OH. According to conformational-energy computations the presence of *gem*-dialkylation at the α-carbon in the Aib residue results in a severe restriction of its conformational freedom (Paterson, Rumsey, Benedetti, Némethy & Scheraga, 1981). The structure of an N^{α}-protected amino acid allows investigation of the conformational preferences of the Aib residue without the influence of the intramolecular hydrogen bonds which have been shown to characterize Aib-containing peptides (Toniolo *et al.*, 1983). Interestingly, the N-terminal part of many peptaibol antibiotics (alamethicin, hypelcin, trichotoxin, suzukacillin) is characterized by the Ac-Aib- sequence (Toniolo *et al.*, 1983). On the other hand, the study of N^{α}-trifluoroacetylated amino-acid derivatives and peptides is of special interest, since they are potent inhibitors of proteolytic enzymes, the protecting group forcing the inhibitor to bind in a special mode to the active site of the enzyme (Hughes, Sieker, Bieth & Dimicoli, 1982).

Experimental. Colourless, rhombic crystals (0·3 × 0·3 × 0·5 mm) of Ac-Aib-OH (Levene & Steiger, 1931; Balasubramanian, Kendrick, Taylor, Marshall, Hall, Vodyanoy & Reusser, 1981; Leibfritz, Haupt, Dubischar, Lachmann, Oekonomopulos & Jung, 1982) obtained from an acetone solution by slow evaporation. Lattice parameters obtained from 25 reflections in θ range 7–14°. No absorption correction. Max. *h,k,l* measured were 11, 9, and 10, respectively. Three standard reflections with 1% intensity variation used to check the electronic stability of the instruments. 1398 independent reflections measured on a Philips PW 1100 four-circle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation, range $4 < 2\theta < 50°$. Structure was solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined by full-matrix least squares on *F* with anisotropic thermal parameters for all non-H atoms ($w = 1$). All H atoms localized on difference Fourier map and refined isotropically. For all calculations *SHELX*76 (Sheldrick, 1976) used. Final *R* for 1053 observed reflections with $I > 3\sigma(I)$ 0·042, $S = 0{\cdot}43$. $(\Delta/\sigma)_{\max}$ in final refinement cycle for non-H atoms 0·06. Max. and min. heights in final difference Fourier synthesis 0·23 and −0·020 e Å^{-3}. Scattering factors for all atomic species from *International Tables for X-ray Crystallography* (1974).

Colourless, polyhedric crystals (0·2 × 0·2 × 0·2 mm) of F_3Ac-Aib-OH (Leplawy, Jones, Kenner & Sheppard, 1960; Leibfritz *et al.*, 1982) obtained from an acetone solution by slow evaporation. Lattice parameters obtained from 24 reflections in θ range 7–15°. No absorption correction. Max. *h,k,l* 18, 14, and 12, respectively. Three standard reflections with 5% intensity variation used to check the electronic stability of the instruments. 1842 independent reflections measured on the same diffractometer and using the same radiation as above to $2\theta = 50°$, θ–2θ scan mode. In subsequent *E* map, O, C and N atoms

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* Linear Oligopeptides. 120. Part 119: Becker, Freer, Toniolo & Balaram (1984).

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localized. In difference Fourier map F atoms found statistically localized essentially in three positions. O, C and N refined anisotropically by full-matrix least squares on F ($w = 1$). All H atoms found on the difference Fourier map and refined isotropically. For all calculations the same program as above was used. Final R for 1121 observed reflections with $I > 3\sigma(I)$ 0·085 (this value is ascribed to the disorder of the F atoms), $S = 1{\cdot}34$. $(\Delta/\sigma)_{\max}$ in final refinement cycle for F atoms 0·5, 0·05 for other non-H atoms. Max. and min. heights in final difference Fourier synthesis 0·50 and $-0{\cdot}37$ e Å^{-3}. The source of atomic scattering factors was the same as above.

Discussion. Atomic coordinates and isotropic thermal parameters for the non-H atoms of Ac-Aib-OH and the three disordered conformations of F_3Ac-Aib-OH are listed in Table 1.* Selected bond lengths and bond angles are given in Table 2. Figs. 1(*a*) and 1(*b*) illustrate the molecular structures of Ac-Aib-OH and one possible conformation of F_3Ac-Aib-OH, respectively.

The rotational disorder, characteristic of the trifluoroacetamido group (Barone, Bavoso, Benedetti, Di Blasio, Grimaldi, Lelj, Pavone, Pedone, Bonora, Toniolo, Lingham & Hardy, 1984; Kalyanaraman, Kispert & Atwood, 1978), unless rigidly bound in the active site of an enzyme (Hughes *et al.*, 1982), is found also in F_3Ac-Aib-OH.

Bond lengths and bond angles of Ac-Aib-OH and F_3Ac-Aib-OH compare well with those found in other acetamido (Chen & Parthasarathy, 1978; Chakrabarti & Dunitz, 1982), trifluoroacetamido (Kalyanaraman *et al.*, 1978; Weinstein & Leiserowitz, 1980; Barone *et al.*, 1984) and Aib derivatives (Paterson *et al.*, 1981) (Table 2).

The dihedral angles between the average planes of the amide and carboxylic acid groups of Ac-Aib-OH and F_3Ac-Aib-OH are 101·1 (3) and 73·0 (6)°, respectively, in agreement with one of the observed preferences for N^{α}-acylated α-amino acids (Chen &

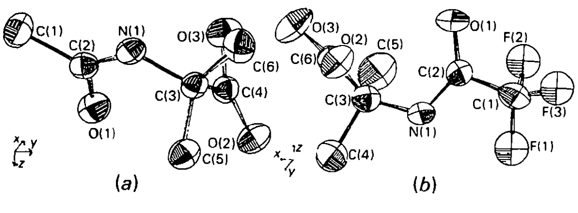

Fig. 1. Molecular structure with the numbering of the atoms of: (*a*) Ac-Aib-OH and (*b*) one possible conformation of F_3Ac-Aib-OH.

Table 1. *Atomic coordinates and isotropic thermal parameters* (Å^2) *for the non-*H *atoms* (*with e.s.d.'s in parentheses*)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$ p.p. = occupancy.

Ac-Aib-OH

	x	y	z	$U_{\rm eq}$
O(1)	0·6572 (2)	0·0192 (3)	0·8266 (2)	0·0410
O(2)	0·6863 (2)	0·4152 (3)	0·9186 (2)	0·0435
O(3)	0·6207 (2)	0·3605 (3)	0·6776 (2)	0·0457
N(1)	0·4393 (2)	0·1212 (3)	0·7046 (2)	0·0325
C(1)	0·4929 (4)	−0·1534 (5)	0·6392 (4)	0·0489
C(2)	0·5366 (3)	0·0016 (4)	0·7303 (3)	0·0330
C(3)	0·4639 (3)	0·2742 (3)	0·7918 (3)	0·0307
C(4)	0·6047 (3)	0·3528 (3)	0·8053 (3)	0·0321
C(5)	0·4605 (4)	0·2366 (4)	0·9447 (3)	0·0402
C(6)	0·3455 (3)	0·3963 (5)	0·7086 (4)	0·0462

F_3Ac-Aib-OH

	x	y	z	p.p.%	$U_{\rm iso}/U_{\rm eq}$
F(1)	0·3482 (7)	−0·0187 (11)	0·1942 (10)	46	0·0672
F(2)	0·3729 (13)	−0·0621 (17)	0·3858 (18)	28	0·0786
F(3)	0·4154 (11)	0·1274 (15)	0·3205 (19)	27	0·0734
F(21)	0·4050 (7)	−0·0057 (12)	0·4055 (9)	45	0·0706
F(22)	0·3982 (11)	0·1056 (16)	0·2372 (20)	30	0·0900
F(23)	0·3365 (14)	−0·0770 (22)	0·2539 (30)	25	0·0997
F(31)	0·3719 (8)	0·0410 (14)	0·1938 (11)	37	0·0664
F(32)	0·3368 (11)	−0·1088 (4)	0·3329 (21)	30	0·0866
F(33)	0·4221 (9)	0·0546 (15)	0·3753 (15)	33	0·0754
O(1)	0·2572 (3)	0·0916 (5)	0·4821 (4)	100	0·0735
O(2)	0·0837 (3)	−0·0123 (3)	0·3856 (4)	100	0·0542
O(3)	0·0179 (3)	0·1397 (4)	0·4670 (4)	100	0·0651
N(1)	0·2118 (3)	0·1130 (5)	0·2712 (5)	100	0·0461
C(1)	0·3520 (5)	0·0238 (9)	0·3132 (7)	100	0·0837
C(2)	0·2676 (4)	0·0803 (6)	0·3632 (5)	100	0·0521
C(3)	0·1283 (4)	0·1706 (5)	0·3034 (5)	100	0·0455
C(4)	0·0769 (5)	0·1842 (9)	0·1740 (8)	100	0·0672
C(5)	0·1436 (6)	0·2861 (6)	0·3644 (9)	100	0·0729
C(6)	0·0745 (4)	0·0933 (5)	0·3935 (5)	100	0·0421

Table 2. *Bond lengths* (Å) *and bond angles* (°) (*with e.s.d.'s in parentheses*)

Ac-Aib-OH

C(1)—C(2)	1·496 (4)	C(2)—O(1)	1·241 (3)
C(2)—N(1)	1·333 (4)	N(1)—C(3)	1·460 (3)
C(3)—C(4)	1·524 (4)	C(3)—C(5)	1·528 (4)
C(3)—C(6)	1·529 (4)	C(4)—O(2)	1·212 (3)
C(4)—O(3)	1·312 (3)		

C(1)—C(2)—O(1)	122·1 (3)	C(1)—C(2)—N(1)	116·9 (3)
O(1)—C(2)—N(1)	121·0 (3)	C(2)—N(1)—C(3)	122·9 (2)
N(1)—C(3)—C(4)	110·6 (2)	N(1)—C(3)—C(5)	109·6 (2)
N(1)—C(3)—C(6)	107·6 (2)	C(4)—C(3)—C(6)	108·0 (2)
C(5)—C(3)—C(6)	110·0 (3)	C(3)—C(4)—O(2)	123·5 (2)
C(3)—C(4)—O(3)	112·5 (2)	O(2)—C(4)—O(3)	123·7 (3)
C(4)—C(3)—C(5)	111·0 (2)		

One possible conformation of F_3Ac-Aib-OH

F(1)—C(1)	1·301 (11)	N(1)—C(3)	1·473 (7)
F(2)—C(1)	1·289 (17)	C(3)—C(4)	1·530 (9)
F(3)—C(1)	1·555 (18)	C(3)—C(5)	1·511 (9)
C(1)—C(2)	1·529 (9)	C(3)—C(6)	1·524 (8)
C(2)—O(1)	1·217 (7)	C(6)—O(2)	1·253 (6)
C(2)—N(1)	1·314 (7)	C(6)—O(3)	1·259 (6)

F(1)—C(1)—C(2)	115·7 (7)	F(2)—C(1)—C(2)	111·1 (9)
F(3)—C(1)—C(2)	99·3 (9)	C(1)—C(2)—O(1)	118·8 (6)
C(1)—C(2)—N(1)	115·7 (5)	O(1)—C(2)—N(1)	125·5 (5)
C(2)—N(1)—C(3)	122·2 (5)	N(1)—C(3)—C(4)	107·3 (5)
N(1)—C(3)—C(5)	111·8 (5)	N(1)—C(3)—C(6)	108·5 (5)
C(4)—C(3)—C(6)	107·4 (5)	C(5)—C(3)—C(6)	112·2 (5)
C(4)—C(3)—C(5)	109·4 (7)	C(3)—C(6)—O(2)	119·6 (5)
C(3)—C(6)—O(3)	117·2 (5)	O(2)—C(6)—O(3)	123·0 (5)
F(2)—C(1)—F(3)	115·8 (12)	F(1)—C(1)—F(3)	111·9 (10)
F(1)—C(1)—F(2)	103·6 (13)		

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39800 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Parthasarathy, 1978). The secondary amide torsion angle ω (IUPAC–IUB Commission on Biochemical Nomenclature, 1970) is 175·7 (4) and −178·9 (6)° (the usual *trans* conformation) for Ac-Aib-OH and F_3Ac-Aib-OH, respectively. In both compounds the Aib residue is folded, the set of φ,ψ_T (Chen & Parthasarathy, 1978) torsion angles [49·0 (6) and 47·3 (5)° for Ac-Aib-OH, and −58·4 (7) and −28·6 (7)° for F_3Ac-Aib-OH] falling in the region of the Ramachandran map where α- and 3_{10}-helical structures are found.

There are no intramolecular hydrogen bonds in Ac-Aib-OH. Rather, the molecules are held together in the most common arrangement of N^{α}-acylated α-amino acids (Berkovitch-Yellin, Ariel & Leiserowitz, 1983), *i.e.* by the formation of a network of O—H···O=C(amide) and N—H···O=C(carboxylic acid) intermolecular hydrogen bonds (Fig. 2*a*). The O(3)···O(1)($\frac{3}{2}-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$) and N(1)···O(2)($x-\frac{1}{2}$, $\frac{1}{2}-y$, $z-\frac{1}{2}$) distances are 2·606 (3) and 3·01 (1) Å, respectively, falling within the most probable ranges for the length of an O—H···O (Brown, 1976; Mitra & Ramakrishnan, 1977) and an N—H···O (Ramakrishnan & Prasad, 1971) hydrogen bond, respectively. The O(3)—H···O(1) and N(1)—H···O(2) angles have values of 169 (4) and 163 (4)°, respectively. This intermolecular hydrogen-bonding scheme compares well with the solid-state IR absorption data: absence of the —OH stretching mode, 3348 cm^{-1} (hydrogen-bonded NH), 1709 cm^{-1} (hydrogen-bonded carbonyl of carboxylic acid group), and 1626–1615 cm^{-1} (hydrogen-bonded carbonyl of the acetamido group) (Benedetti, Di Blasio, Pavone, Pedone, Toniolo & Bonora, 1981; Valle *et al.*, 1984).

A pair of F_3Ac-Aib-OH molecules are held together across a crystallographic centre of symmetry by the formation of two intermolecular hydrogen bonds of the O—H···O=C(carboxylic acid) type (Fig. 2*b*). Their O(2)···O(3)($-x$, $-y$, $1-z$) distance is 2·615 (6) Å (Brown, 1976; Mitra & Ramakrishnan, 1977). There are additional intermolecular hydrogen bonds of the N—H···O=C(amide) type, their N(1)···O(1)($\frac{1}{2}-x$, y, $z-\frac{1}{2}$) distance being 2·966 (7) Å (Ramakrishnan & Prasad, 1971), resulting in the formation of linear chains of dimers. The O(2)—H···O(3) and N(1)—H···O(1) angles have values of 162 (4) and 162 (6)°, respectively. This hydrogen-bonding scheme, unusual for an N^{α}-acylated α-amino acid (Berkovitch-Yellin *et al.*, 1983), together with the known inductive effect of the halo-substituents (Nyquist, 1963; Krueger & Smith, 1967; Moussebois, Heremans, Osinski & Rennerts, 1976; Tesch & Schulz, 1981), is fully in keeping with our solid-state IR absorption data: absence of the —OH stretching mode, 3312 cm^{-1} (hydrogen-bonded NH), 1722 cm^{-1} and 1706 cm^{-1} (hydrogen-bonded carbonyls of the carboxylic acid and trifluoroacetamido groups) (Valle *et al.*, 1984).

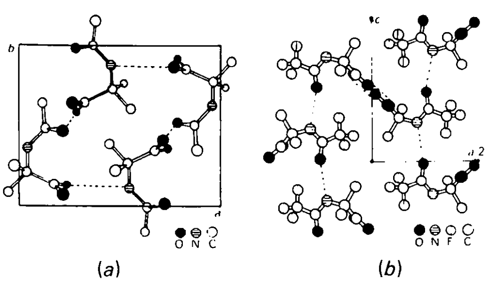

Fig. 2. Molecular packing and intermolecular hydrogen-bonding scheme for: (*a*) the Ac-Aib-OH molecules projected down the *c* axis and (*b*) one possible conformation of the F_3Ac-Aib-OH molecules viewed down the *b* axis. Hydrogen bonds are shown as dashed lines.

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Structure of 5,6,7,8-Tetrafluoro-9-methyl-1,4-dihydro-1,4-iminonaphthalene, $C_{11}H_7F_4N$

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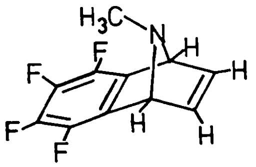
Abstract. $M_r = 229{\cdot}18$, monoclinic, $P2_1/n$, $a = 6{\cdot}258\,(4)$, $b = 31{\cdot}85\,(1)$, $c = 9{\cdot}481\,(6)$ Å, $\beta = 99{\cdot}71\,(5)°$, $V = 1862{\cdot}60$ Å^3, $Z = 8$, $D_x = 1{\cdot}63$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 1{\cdot}46$ cm^{-1}, $F(000) = 928$, $T = 115$ K, $R = 0{\cdot}057$ for 1687 unique observed reflections. The distances from the *N*-methyl carbon atom to the center of the benzene ring in the two independent molecules are 3·608 (8) and 3·616 (11) Å; the corresponding imine bridge bond angles are 95·0 (7) and 96·0 (4)°, which are small for an sp^3-hybridized N atom.

Introduction. The crystal structure determination of the title compound was undertaken in continuation of our studies of the chemical and physical properties of arenimines (Gribble, Sibi, Kumar & Kelly, 1983; LeHoullier & Gribble, 1983). It was of particular interest to establish the configuration of the methyl group in the solid state and to determine the imine bridge bond angle in this presumably strained molecule.



Experimental. Preparation described by Gribble, Allen, LeHoullier, Eaton, Easton, Slayton & Sibi (1981). Recrystallization from hexane; colorless, fragment cut from large irregular single crystal, 0·25 × 0·50 × 0·50 mm; Syntex $P\bar{1}$ diffractometer equipped with variable-temperature device (Strouse, 1976); graphite monochromator; unit-cell parameters by least-squares refinement of 15 reflections ($17{\cdot}50 \le 2\theta \le 27{\cdot}57°$), θ–2θ scan, 24·0° min^{-1}, $2\theta_{\max} = 45°$ for range $0 \le h \le 6$, $0 \le k \le 33$, $-10 \le l \le 10$; 3 reflections monitored every 97 reflections with no significant variation; 2863 measured intensities, 2453 unique, 1687 with $I > 3\sigma(I)$, 766 unobserved; Lorentz and polarization but no absorption correction. Structure solved by direct methods; N(2), C(8), C(11), C(27), C(28), C(30) and all hydrogen atoms located in difference Fourier maps. Refinement included positional and anisotropic thermal parameters for all non-hydrogen atoms in high-occupancy fragments. Hydrogen atoms included in structure factor calculation. Difference maps revealed disorder in imine bridge and ethylene fragments of both molecules in asymmetric unit. Low-occupancy fragments labeled *L*1 [consisting of N(1*D*), C(7*D*)–C(11*D*) and H(7*D*)–H(11*D*)] and *L*2 [consisting of N(2*D*), C(26*D*)–C(30*D*) and H(26*D*)–H(30*D*)] located and fragment *L*2 included in structure factor calculation. Fragment *L*1 non-hydrogen atoms with isotropic temperature factors included in refinement with high-occupancy fragments *H*1 [consisting of N(1), C(7)–C(11) and H(7)–H(11)] and *H*2 [consisting of N(2), C(26)–C(30) and H(26)–H(30)]. Sums of occupancies of two fragments in each molecule constrained to unity. Refined occupancies of *H*1 and *H*2 fragments 0·70 (1) and 0·94 (1), respectively. Refinement in $P2_1/m$ did not account for disorder nor were

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