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L-Aspartyl(β-benzyl ester)glycylglycine Methyl Ester Trifluoroacetic Acid [L-Asp(β-Bzl)-Gly-Gly-OMe.Tfa]

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Abstract. L-α-Aspartiumylglycylglycine β-benzyl methyl ester trifluoroacetate, $C_{16}H_{22}N_3O_6^+.C_2F_3O_2^-$, M_r = 465·39, orthorhombic, $P2_12_12_1$, a = 5·425 (2), b = 12·159 (1), c = 32·925 (8) Å, V = 2171 (1) Å^3, Z = 4, D_x = 1·42 Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ(Cu $K\alpha$) = 1·1 mm^{-1}, F(000) = 968, room temperature, final R = 0·071 for 1550 observed reflections. The title compound consists of the trifluoroacetate anion and the peptide with the amino terminus protonated. The conformation of the peptide linkages is *trans* and the main-chain conformation of the tripeptide is not fully extended. The packing is determined by extensive hydrogen bonding with every available donor atom participating.

Introduction. Peptides containing a β-blocked aspartyl residue easily cyclize forming a substituted succinimide (Bodansky & Kwei, 1978). From a structural point of view the formation of this cycle requires that the dihedral angle ψ of the aspartyl residue (N_i—C_i—C_i—N_{i+1}) assumes a value close to −120°, which falls in a disallowed region of the Ramachandran map for an L residue. It has been suggested that the deamidation of an asparaginyl side chain in proteins may occur through the formation of the cyclic imide as intermediate (Aswad, 1984). As a part of our ongoing research into structural properties of β-blocked aspartyl peptides and aminosuccinyl peptides (Capasso, Mattia, Mazzarella & Zagari, 1984*a*,*b*; Capasso, Mazzarella, Sica & Zagari, 1984), we have synthesized and studied, by X-ray analysis, the tripeptide L-Asp(β-Bzl)-Gly-Gly-OMe.Tfa.

Experimental. Crystals from aqueous solution, 0·80 × 0·50 × 0·1 mm; Enraf–Nonius CAD-4F diffractometer, Ni-filtered Cu $K\alpha$ radiation; lattice parameters from 20 reflections ($21 < \theta < 30°$); data collection: ω scan, two monitoring reflections (2% variation); 2421 independent reflections with $\theta \leq 70°$, $0 \leq h \leq 6$, $0 \leq k \leq 14$, $0 \leq l \leq 39$, 1554 with $I > 2{\cdot}5\sigma(I)$; Lp correction, absorption ignored. Structure solved by *MULTAN*80 (Main *et al.*, 1980); anisotropic full matrix (on F), H atoms from geometrical considerations, isotropic with the same B_{eq} as the atoms to which they are bonded, not refined; four reflections (110, 002, 103, 006 measured improperly due to asymmetric background) excluded from final cycles of refinement. Final R = 0·071, wR = 0·074, $w = 1/\sigma^2(F_o)$, S = 3·28; final $(\Delta/\sigma)_{max}$ = 0·04, max. and min. heights in final Δρ map 0·31 and −0·26 e Å^{-3}; scattering factors from *International Tables for X-ray Crystallography* (1974); Enraf–Nonius (1979) *SDP* software and PDP 11/34 computer of the Centro di Metodologie Chimico-Fisiche dell'Università di Napoli.

Discussion. A view of the asymmetric unit, which consists of the trifluoroacetate anion and the tripeptide with the amino terminus protonated, is shown in Fig. 1. The final positional parameters together with their e.s.d.'s are listed in Table 1. The relevant bond lengths and angles are in Table 2.*

An inspection of the geometrical parameters of the peptide chain reveals, as a whole, good agreement with those of the related structure of the L-Asp-Gly dipeptide (Eggleston, Valente & Hodgson, 1981) and with the average values reported by Benedetti (1977). The only meaningful difference is found in the length [1·376 (6) Å] of the peptide bond C(8)—N(2) between the aspartyl and glycyl residues, which is 0·04 Å longer than the expected value. It is interesting to note that similar lengthening of the C(8)—N(2) bond is observed

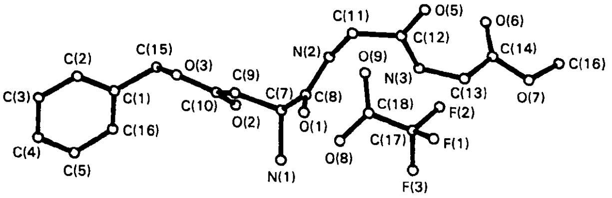

Fig. 1. The observed conformation of L-Asp(β-Bzl)-Gly-Gly-OMe.Tfa with the numbering scheme.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43685 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2)

$$B_{\text{eq}} = \tfrac{4}{3}\textstyle\sum_i \sum_j b_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
F(1)	0·0251 (21)	0·6180 (6)	0·1299 (2)	20·5 (3)
F(2)	0·2515 (15)	0·4876 (4)	0·1374 (1)	12·8 (2)
F(3)	0·3662 (16)	0·6454 (6)	0·1531 (2)	20·5 (2)
O(1)	0·5066 (9)	0·5037 (3)	0·2688 (1)	5·2 (1)
O(2)	1·2364 (10)	0·3695 (4)	0·3556 (2)	7·4 (1)
O(3)	0·9716 (11)	0·3608 (4)	0·4078 (1)	6·7 (1)
O(5)	0·2916 (9)	0·2216 (3)	0·1716 (1)	5·4 (1)
O(6)	0·8242 (11)	0·1295 (3)	0·1292 (1)	6·4 (1)
O(7)	0·9341 (13)	0·2492 (4)	0·0814 (1)	9·1 (2)
O(8)	0·0718 (10)	0·6498 (3)	0·2173 (1)	6·5 (1)
O(9)	−0·0055 (11)	0·4719 (3)	0·2048 (1)	6·6 (1)
N(1)	0·9850 (12)	0·5487 (4)	0·2956 (1)	4·7 (1)
N(2)	0·6164 (11)	0·3227 (4)	0·2601 (2)	4·6 (1)
N(3)	0·6496 (12)	0·3133 (4)	0·1760 (2)	5·1 (1)
C(1)	1·2072 (16)	0·3822 (6)	0·4690 (2)	6·4 (2)
C(2)	1·0657 (22)	0·3841 (7)	0·5017 (2)	9·1 (3)
C(3)	1·1114 (25)	0·4476 (8)	0·5345 (3)	11·3 (3)
C(4)	1·3147 (22)	0·5158 (7)	0·5336 (3)	9·7 (3)
C(5)	1·4589 (24)	0·5157 (10)	0·5015 (3)	13·4 (4)
C(6)	1·0820 (27)	0·1647 (7)	0·0614 (3)	12·1 (4)
C(7)	0·8728 (13)	0·4364 (5)	0·3015 (2)	4·3 (1)
C(8)	0·6489 (14)	0·4273 (5)	0·2750 (2)	4·4 (1)
C(9)	0·8149 (14)	0·4175 (5)	0·3458 (2)	4·8 (2)
C(10)	1·0309 (14)	0·3815 (5)	0·3694 (2)	4·8 (2)
C(11)	0·4033 (14)	0·2901 (5)	0·2366 (2)	4·6 (2)
C(12)	0·4471 (13)	0·2702 (5)	0·1926 (2)	4·7 (2)
C(13)	0·6810 (17)	0·3183 (5)	0·1333 (2)	5·8 (2)
C(14)	0·8206 (18)	0·2208 (5)	0·1159 (2)	6·2 (2)
C(15)	1·1628 (22)	0·3104 (6)	0·4335 (2)	8·8 (2)
C(16)	1·4089 (22)	0·4474 (9)	0·4690 (3)	10·9 (3)
C(17)	0·1812 (24)	0·5743 (6)	0·1556 (2)	10·0 (3)
C(18)	0·0765 (16)	0·5645 (6)	0·1961 (2)	6·0 (2)

in all the structures of aminosuccinyl-containing peptides (Capasso *et al.*, 1984, 1984*a*,*b*; Capasso, Mazzarella, Sica & Zagari, in preparation), where this bond is included in a five-membered-ring structure. The geometries of the trifluoroacetate anion and of the side chain of the aspartyl residue show larger discrepancies, which are a consequence of the lack of accuracy owing to their substantial thermal motion. The values of the B_{eq}'s, particularly for the CF_3 group, are indeed indicative of some disordering in the crystal and can justify the rather high value of the final R index.

The principal torsion angles of the molecule are shown in Table 3. Both peptide groups have the *trans* conformation. For one group [$\omega = 174·6\ (12)°$] no atom deviates more than 0·037 Å from the least-squares plane [C(7)C(8)O(1)N(2)C(11)]; whereas for the other group [$\omega = -166·7\ (13)°$] the deviation from planarity is more severe, with one atom deviating 0·092 Å from the least-squares plane [C(11)C(12)-O(5)N(3)C(13)].

The dihedral angles ψ_1, φ_2, ψ_2 (145·5, 108·5 and −19·3°) are reminiscent of those found for the residues in positions 2 and 3 of a type II β-turn conformation. For a sequence of four residues, this reverse turn is characterized by the dihedral angles $\varphi = -60$, $\psi = 120°$ and $\varphi = 80$, $\psi = 0°$ for the second and third residue, respectively, and is stabilized by an intramolecular hydrogen bond between the CO group of the first residue and the NH group of the fourth. In our case, in the absence of the first residue, the φ_1 angle is not defined and the hydrogen bond cannot be formed. Nevertheless, the Asp-Gly sequence adopts a folded conformation resembling a type II β turn.

The packing is stabilized by an intermolecular hydrogen-bonding network which engages all hydrogenated N atoms. There are several charged [O(8) and O(9)] and uncharged [O(1), O(5) and O(6)] O atoms surrounding the protonated terminal N(1) atom at a distance less than 3·15 Å. After consideration of the disposition of the atoms, it was concluded that only N(1)···O(5$^{\text{i}}$), N(1)···O(6$^{\text{ii}}$) and N(1)···O(8$^{\text{iii}}$), with separations of 2·80 (1), 2·86 (1) and 2·89 (1) Å, respectively, have a geometry compatible with hydrogen bonding. In addition, two hydrogen bonds are formed between the peptide and the anion joining N(2) to O(8$^{\text{iv}}$) and N(3) to O(9$^{\text{iii}}$), with separations of

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

F(1)—C(17)	1·310 (13)	N(2)—C(11)	1·445 (9)
F(2)—C(17)	1·270 (9)	N(3)—C(12)	1·334 (9)
F(3)—C(17)	1·327 (13)	N(3)—C(13)	1·417 (8)
O(1)—C(8)	1·225 (8)	C(1)—C(2)	1·323 (12)
O(2)—C(10)	1·213 (9)	C(1)—C(15)	1·478 (10)
O(3)—C(15)	1·472 (11)	C(1)—C(16)	1·351 (14)
O(3)—C(10)	1·328 (8)	C(2)—C(3)	1·351 (12)
O(5)—C(12)	1·240 (8)	C(3)—C(4)	1·380 (16)
O(6)—C(14)	1·194 (8)	C(4)—C(5)	1·317 (15)
O(7)—C(6)	1·460 (12)	C(5)—C(16)	1·381 (14)
O(7)—C(14)	1·339 (9)	C(7)—C(8)	1·499 (10)
O(8)—C(18)	1·250 (8)	C(7)—C(9)	1·510 (9)
O(9)—C(18)	1·245 (8)	C(9)—C(10)	1·473 (10)
N(1)—C(7)	1·507 (8)	C(11)—C(12)	1·489 (9)
C(13)—C(14)	1·519 (10)	C(17)—C(18)	1·455 (11)
N(2)—C(8)	1·376 (7)		
C(10)—O(3)—C(15)	117·0 (10)	O(3)—C(10)—C(9)	111·5 (10)
C(6)—O(7)—C(14)	117·0 (12)	N(2)—C(11)—C(12)	115·9 (9)
C(8)—N(2)—C(11)	123·2 (9)	O(5)—C(12)—N(3)	121·3 (10)
C(12)—N(3)—C(13)	121·5 (10)	O(5)—C(12)—C(11)	120·7 (10)
C(2)—C(1)—C(15)	124·0 (13)	N(3)—C(12)—C(11)	117·8 (10)
C(2)—C(1)—C(16)	117·3 (14)	N(3)—C(13)—C(14)	113·6 (11)
C(15)—C(1)—C(16)	118·6 (13)	O(6)—C(14)—O(7)	122·9 (12)
C(1)—C(2)—C(3)	123·7 (16)	O(6)—C(14)—C(13)	126·6 (12)
C(2)—C(3)—C(4)	118·2 (17)	O(7)—C(14)—C(13)	110·4 (11)
C(3)—C(4)—C(5)	119·5 (17)	O(3)—C(15)—C(1)	108·8 (12)
C(4)—C(5)—C(16)	120·4 (18)	C(1)—C(16)—C(5)	120·8 (17)
N(1)—C(7)—C(8)	108·6 (9)	F(1)—C(17)—F(2)	103·2 (14)
N(1)—C(7)—C(9)	110·3 (9)	F(1)—C(17)—F(3)	100·7 (14)
C(8)—C(7)—C(9)	112·5 (9)	F(1)—C(17)—C(18)	111·9 (14)
O(1)—C(8)—N(2)	124·1 (10)	F(2)—C(17)—F(3)	106·6 (14)
O(1)—C(8)—C(7)	123·5 (10)	F(2)—C(17)—C(18)	118·7 (14)
N(2)—C(8)—C(7)	112·3 (9)	F(3)—C(17)—C(18)	113·9 (14)
C(7)—C(9)—C(10)	113·0 (10)	O(8)—C(18)—O(9)	127·9 (12)
O(2)—C(10)—O(3)	123·8 (11)	O(8)—C(18)—C(17)	116·9 (12)
O(2)—C(10)—C(9)	124·6 (11)	O(9)—C(18)—C(17)	115·2 (12)

Table 3. *Some observed dihedral angles* (°) *for* L-*Asp-(β-Bzl)-Gly-Gly-*O*Me.Tfa*

ψ_1	N(1)—C(7)—C(8)—N(2)	145·5 (11)
ω_1	C(11)—N(2)—C(8)—C(7)	174·6 (12)
φ_2	C(8)—N(2)—C(11)—C(12)	108·5 (11)
ψ_2	N(2)—C(11)—C(12)—N(3)	−19·3 (10)
ω_2	C(13)—N(3)—C(12)—C(11)	−166·7 (13)
φ_3	C(12)—N(3)—C(13)—C(14)	−93·6 (12)
ψ_3	N(3)—C(13)—C(14)—O(7)	−153·7 (12)
ω_3	C(13)—C(14)—O(7)—C(6)	178·5 (15)
χ_1	C(10)—C(9)—C(7)—N(1)	−82·1 (10)

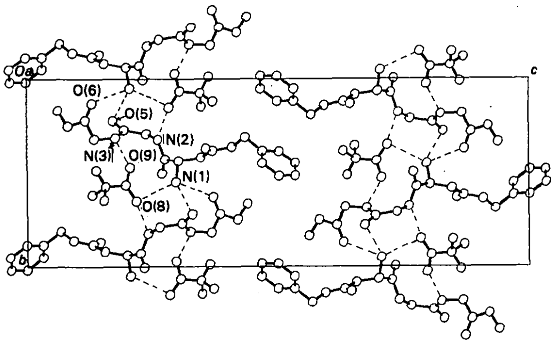

Fig. 2. The crystal structure of L-Asp(β-Bzl)-Gly-Gly-OMe.Tfa as viewed perpendicular to the yz plane. Contacts indicative of hydrogen bonding are shown by dashed lines.

2·80 (1) and 2·85 (1) Å respectively [symmetry codes: (i) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $2-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $1+x, y, z$; (iv) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$]. The hydrogen-bonding network gives rise to layers normal to the c axis (Fig. 2). In each layer the hydrophilic cores of adjacent molecules are linked together, intercalating the trifluoroacetate anion, whereas the terminal benzyl and methyl hydrophobic groups protrude alternately from the surface of the layer. The layers are held together in the crystals only by van der Waals forces between hydrophobic groups.

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Structures of New Salts: *S*-Methylthiouronium–TCNQ (I) and *Se*-Methylselenouronium–TCNQ (II)*

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Abstract. Isostructural salts MT–TCNQ (I), $C_{14}H_{11}N_6S$, and MS–TCNQ (II), $C_{14}H_{11}N_6Se$, are monoclinic, $P2_1/c$, $Z = 4$. (I): $M_r = 295·35$, $a = 11·005$ (2), $b = 12·305$ (3), $c = 11·112$ (3) Å, $\beta = 100·98$ (2)°, $V = 1477·2$ Å^3, $D_x = 1·33$ g cm^{-3}, μ(Mo $K\alpha$) = 1·7 cm^{-1}, $F(000) = 612$, $R = 0·042$ for 917 observed reflections. (II): $M_r = 342·24$, $a = 10·984$ (2), $b = 12·269$ (2), $c = 11·191$ (2) Å, $\beta = 100·90$ (1)°, $V = 1480·9$ Å^3, $D_x = 1·54$ g cm^{-3}, μ(Mo $K\alpha$) = 18·7 cm^{-1}, $F(000) = 684$, $R = 0·049$ for 1349 observed reflections. Room temperature, λ(Mo $K\alpha$) = 0·71069 Å. Structures contain isolated pairs of planar TCNQ radical anions with mean interplanar distance 3·40 Å for both salts. Anions and cations lie in different layers parallel to the (100) plane. Hydrogen bonds are found between NH_2 groups of cations and nitrogen atoms of TCNQ anions.

Introduction. A considerable number of TCNQ salt structures have been reported elsewhere (Shibaeva, 1981). New salts of TCNQ with cations based on thio- and selenouronium [$NH_2C(=X)NH_2$, where X is S or Se] were prepared in the present work. Their synthesis, electrical properties at room temperature and structures are described below. The importance of these new salts lies in their practical use as materials for gas analysers.

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* TCNQ = 2,2′-(2,5-Cyclohexadiene-1,4-diylidene)bispropanedinitrile.

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