The Crystal Structure of *N*-(*t*-Butoxycarbonyl)-L-methionylglycine Benzyl Ester

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The crystal structure of *N*-(*t*-butoxycarbonyl)-L-methionylglycine benzyl ester has been determined. The crystal data are: $P2_1$, $a=15.884(4)$, $b=5.083(2)$, $c=13.296(3)$ Å, $\beta=94.54(2)°$, $Z=2$. The final R is 0.055 for 1518 reflections. In the methionyl residue the C^{α}–C^{β} bond is longer than the C^{β}–C^{γ} bond. The tendency is consistent with that found in the other methionine compounds. The methionyl side chain has the most stable trans zig-zag conformation ($\chi^1=-73.2$, $\chi^2=175.3$, and $\chi^3=174.9°$). The peptide main chains are packed in a parallel β-sheet structure, the torsion angles (ϕ,ψ) of the methionyl residue being (-110.6, $108.3°$).

The structure analyses of proteins have shown that the secondary structures, such as, α-helix,[1] β-structure,[2] and β-turn[3] play an important role in the folding of proteins. On the other hand, in the crystalline state many oligopeptides are also found to have either one of the secondary structures.[4] This fact suggests that the secondary structures are significant in the peptide structures of not only polymers but also oligomers. Thus, the precise parameters of the secondary structures obtained by the crystal analyses of oligopeptides are substantially important in the refinements and the model buildings of the protein structures or the structural analyses of fibrous proteins.

In this paper the structure of *N*-(*t*-butoxycarbonyl)-L-methionylglycine benzyl ester(Boc-L-Met-Gly-OBz)† having a parallel β-pleated sheet structure is reported.

Experimental

Boc-L-Met-Gly-OBz was prepared from dicyclohexylammonium *N*-(*t*-butoxycarbonyl)-L-methionate and glycine benzyl ester tosylate in a $CHCl_3$ solution. Needle crystals were obtained from an ethyl acetate–hexane solution. Crystal data are: $C_{19}H_{28}N_2O_5S$, $M.W.=396.50$, $P2_1$, $a=15.884(4)$,

TABLE 1. THE ATOMIC PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS($\times 10^4$)
Thermal parameters are in the form: $\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-\beta_{12}hk-\beta_{13}hl-\beta_{23}kl)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	10888 (1)	2500 (4)	1079 (1)	50 (0)	489 (8)	102 (1)	10 (4)	18 (1)	−98 (5)
C (1)	7553 (4)	7975 (21)	5173 (6)	70 (3)	854 (56)	107 (5)	−155 (28)	45 (7)	−265 (32)
C (2)	8349 (14)	4433 (19)	6123 (6)	473 (44)	423 (44)	66 (5)	−20 (64)	150 (19)	1 (28)
C (3)	9127 (4)	8091 (18)	5404 (5)	63 (3)	694 (48)	112 (5)	123 (23)	−58 (7)	−290 (30)
C (4)	8360 (5)	6321 (15)	5281 (4)	120 (5)	414 (31)	43 (3)	27 (24)	18 (6)	−38 (18)
O (1)	8390 (3)	4611 (8)	4385 (2)	120 (3)	288 (17)	42 (2)	−9 (14)	23 (4)	−34 (11)
C (5)	8425 (3)	5667 (12)	3467 (3)	51 (2)	322 (24)	55 (3)	−34 (15)	4 (4)	−32 (16)
O (2)	8414 (3)	8036 (8)	3273 (3)	105 (3)	250 (18)	66 (2)	−20 (13)	13 (4)	8 (11)
N (1)	8451 (2)	3757 (10)	2766 (3)	51 (2)	308 (19)	52 (2)	0 (15)	−2 (3)	−19 (13)
C (6)	8453 (3)	4351 (11)	1074 (3)	42 (2)	293 (23)	42 (2)	−24 (13)	−4 (3)	−5 (14)
C (7)	9091 (3)	2970 (12)	1229 (3)	43 (2)	362 (25)	58 (3)	−52 (14)	8 (4)	−4 (16)
C (8)	10026 (3)	4287 (13)	1553 (4)	42 (2)	404 (29)	72 (3)	0 (15)	1 (4)	−58 (19)
C (9)	11746 (4)	4591 (15)	1460 (5)	48 (2)	526 (37)	101 (4)	−16 (19)	4 (6)	−19 (25)
C (10)	7616 (3)	3485 (12)	1173 (3)	46 (2)	345 (24)	49 (3)	0 (14)	10 (4)	30 (15)
O (3)	7418 (2)	1139 (8)	1047 (3)	49 (1)	246 (15)	94 (3)	−61 (9)	−10 (3)	−22 (12)
N (2)	7096 (2)	5492 (10)	863 (3)	41 (2)	321 (20)	77 (3)	8 (12)	−18 (4)	−11 (14)
C (11)	6266 (3)	4900 (15)	372 (4)	37 (2)	581 (36)	78 (3)	11 (16)	−6 (4)	−46 (22)
C (12)	6313 (3)	4046 (13)	−696 (4)	43 (2)	379 (28)	71 (3)	26 (16)	−4 (4)	−42 (19)
O (4)	6851 (2)	4530 (11)	−1239 (3)	56 (2)	738 (31)	84 (3)	−101 (14)	23 (3)	−62 (20)
O (5)	5625 (2)	2542 (11)	−978 (2)	52 (1)	620 (25)	69 (2)	−119 (14)	−5 (3)	−45 (15)
C (13)	5535 (4)	1712 (15)	−2032 (4)	71 (3)	505 (35)	62 (3)	−57 (20)	−11 (5)	−62 (20)
C (14)	5120 (4)	3886 (16)	−2684 (4)	60 (3)	533 (32)	53 (3)	−13 (20)	4 (5)	−97 (19)
C (15)	4271 (4)	4419 (20)	−2631 (5)	49 (2)	839 (53)	82 (4)	−88 (23)	17 (5)	−21 (28)
C (16)	3888 (4)	6401 (23)	−3225 (5)	51 (3)	1034 (68)	95 (5)	23 (27)	10 (6)	−108 (34)
C (17)	4339 (4)	7776 (18)	−3892 (5)	81 (4)	599 (40)	82 (4)	104 (25)	−28 (7)	−59 (26)
C (18)	5181 (5)	7172 (17)	−3691 (4)	89 (4)	529 (37)	73 (4)	−36 (26)	13 (6)	32 (23)
C (19)	5565 (4)	5279 (17)	−3360 (4)	59 (3)	625 (37)	67 (4)	0 (21)	24 (5)	−14 (22)

† The abbreviations used in this paper are: Boc-, *N*-(*t*-butoxycarbonyl); Ac-, *N*-acetyl; -OBz, benzyl ester; -OMe, methyl ester; -OEt, ethyl ester; -NMe, *N*-methylamide.

$b=5.083(2)$, $c=13.296(3)$Å, $\beta=94.54(2)°$, $D_m=1.235$, $D_x=1.242$ g cm^{-3}, $Z=2$, μ(Cu $K\alpha$)$=15.7$ cm^{-1}.

The intensity data were collected on a Hilger & Watts four-circle diffractometer, using Ni-filtered Cu Kα radiation. 1518 independent reflections with $2\theta \leq 110°$ were obtained, of which non-zero reflections were 1490. The ω-2θ step scan was adopted. The crystal used for the data collection had the dimensions of $0.09\times0.20\times0.43$ mm. The intensity data were corrected for Lorentz and polarization effects, but an absorption correction was not made.

Structure Determination

The structure was solved by the use of MULTAN.[5] The refinement was carried out by the block-diagonal least-squares method.[6] In the refinement, the function minimized was $\sum w(|F_o|-k|F_c|)^2$. The assignment of weight is; $w=(\sigma^2(F)+a|F_o|+b|F_o|^2)^{-1}$ for $|F_o|>0$ and $w=c$ for $|F_o|=0$, where $\sigma(F)$ is the standard deviation based on the counting statistics, and $a=-0.0479$, $b=0.0045$, and $c=0.3675$. The final R value is 0.055 for all reflections.

The atomic scattering factors were taken from "International Tables for X-Ray Crystallography," Vol. IV.[7] The calculations were carried out on a FACOM 230-75 computer at Nagoya University. The final atomic parameters are listed in Tables 1 and 2.[8]

Table 2. The parameters of hydrogen atoms($\times 10^3$)
The standard deviations are given in parentheses.

	Bonded to	x	y	z
H(1)	C(1)	741(4)	894(18)	575(5)
H(2)	C(1)	706(4)	675(16)	498(5)
H(3)	C(1)	755(4)	911(17)	466(4)
H(4)	C(2)	826(4)	555(20)	673(5)
H(5)	C(2)	873(4)	356(19)	624(4)
H(6)	C(2)	789(4)	379(19)	598(5)
H(7)	C(3)	925(4)	886(18)	605(4)
H(8)	C(3)	905(4)	923(16)	487(5)
H(9)	C(3)	957(4)	668(16)	545(4)
H(10)	N(1)	861(4)	273(19)	292(5)
H(11)	C(6)	857(4)	652(17)	161(4)
H(12)	C(7)	910(4)	300(18)	39(5)
H(13)	C(7)	919(4)	118(18)	146(4)
H(14)	C(8)	1011(4)	457(19)	243(5)
H(15)	C(8)	1001(4)	626(18)	133(5)
H(16)	C(9)	1226(4)	422(17)	96(4)
H(17)	C(9)	1185(4)	443(19)	221(5)
H(18)	C(9)	1164(4)	610(18)	137(4)
H(19)	N(2)	729(4)	683(17)	85(4)
H(20)	C(11)	592(4)	631(17)	43(5)
H(21)	C(11)	597(4)	347(19)	75(5)
H(22)	C(13)	510(4)	−8(18)	−205(5)
H(23)	C(13)	619(4)	122(18)	−231(5)
H(24)	C(15)	396(4)	351(19)	−215(5)
H(25)	C(16)	332(4)	649(18)	−310(4)
H(26)	C(17)	404(4)	890(18)	−434(5)
H(27)	C(18)	542(4)	798(18)	−452(4)
H(28)	C(19)	630(4)	489(18)	−334(5)

Discussion

Bond lengths and angles of non-hydrogen atoms are listed in Table 3. The torsion angles of the peptide chain are shown in Fig. 1, together with the numbering of atoms. The definition of the torsion angles given by IUPAC-IUB Commission on Biochemical Nomenclature[9] is adopted. The stereoscopic view of the molecule drawn by ORTEP II[10] is shown in Fig. 2.

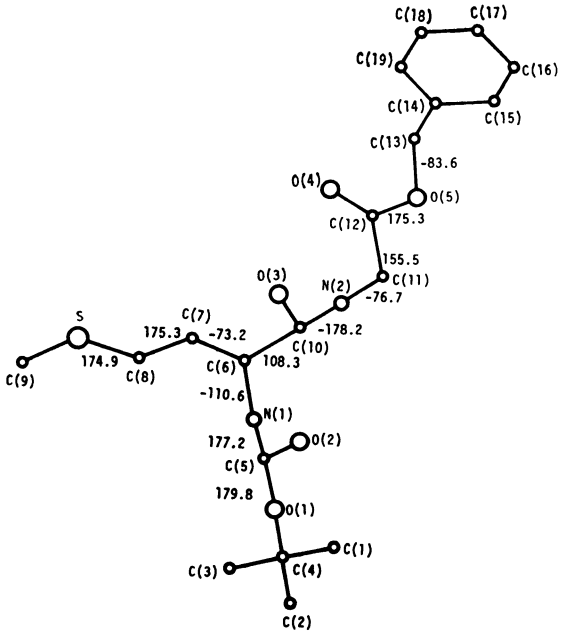

Fig. 1. Torsion angles of the peptide chain. Definitions for these angles are those given by IUPAC-IUB Commission on Biochemical Nomenclature (1970).

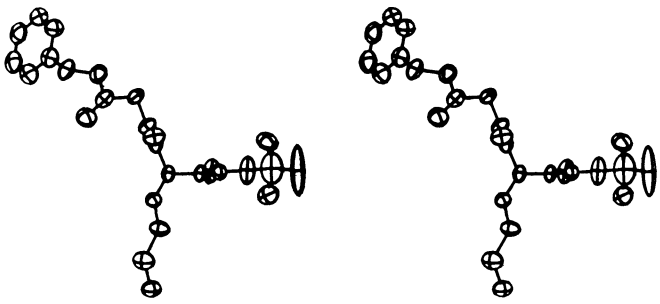

Fig. 2. Stereoscopic view with thermal ellipsoids drawn to enclose 50% probability.

The molecule is constructed with five planar groups, that is, ester I(Boc-L-Met), peptide, ester II(Gly-OBz), phenyl and methionyl side chain groups. The equations of the best planes and the related data are given in Table 4. Each pair of neighboring planes intersect roughly perpendicularly with each other, thus avoiding close contacts between the groups.

In the Boc group, the C(2)–C(4) bond length of 1.470(24) Å is significantly short. This may be attributed to the large thermal vibration of C(2), as shown in Fig. 2. The significant deformation of the bond angles

TABLE 3. THE BOND LENGTHS AND ANGLES FOR NON-HYDROGEN ATOMS

(a) Bond lengths (l/Å)

C(1)–C(4)	1.526(14)	C(2)–C(4)	1.470(24)	C(3)–C(4)	1.508(13)
C(4)–O(1)	1.473(10)	O(1)–C(5)	1.337(9)	C(5)–O(2)	1.221(8)
C(5)–N(1)	1.342(8)	N(1)–C(6)	1.445(8)	C(6)–C(7)	1.539(8)
C(7)–C(8)	1.515(9)	C(8)–S	1.795(7)	S–C(9)	1.765(8)
C(6)–C(10)	1.520(9)	C(10)–O(3)	1.231(8)	C(10)–N(2)	1.349(8)
N(2)–C(11)	1.456(10)	C(11)–C(12)	1.492(10)	C(12)–O(4)	1.186(9)
C(12)–O(5)	1.359(9)	O(5)–C(13)	1.459(10)	C(13)–C(14)	1.515(12)
C(14)–C(15)	1.382(13)	C(15)–C(16)	1.384(16)	C(16)–C(17)	1.371(15)
C(17)–C(18)	1.382(13)	C(18)–C(19)	1.357(13)	C(14)–C(19)	1.379(12)

(b) Bond angles (ϕ/°)

C(1)–C(4)–C(2)	111.3(11)	C(1)–C(4)–C(3)	110.6(8)
C(2)–C(4)–C(3)	111.0(11)	C(1)–C(4)–O(1)	108.9(7)
C(2)–C(4)–O(1)	103.9(11)	C(3)–C(4)–O(1)	110.9(7)
C(4)–O(1)–C(5)	120.8(6)	O(1)–C(5)–N(1)	110.7(6)
O(1)–C(5)–O(2)	125.6(6)	O(2)–C(5)–N(1)	123.7(6)
C(5)–N(1)–C(6)	122.2(5)	N(1)–C(6)–C(7)	111.6(5)
N(1)–C(6)–C(10)	108.9(5)	C(6)–C(7)–C(8)	111.3(5)
C(7)–C(8)–S	110.9(5)	C(8)–S–C(9)	101.1(4)
C(7)–C(6)–C(10)	110.2(5)	C(6)–C(10)–N(2)	114.7(6)
C(6)–C(10)–O(3)	122.9(6)	O(3)–C(10)–N(2)	122.3(6)
C(10)–N(2)–C(11)	119.6(6)	N(2)–C(11)–C(12)	112.0(6)
C(11)–C(12)–O(4)	127.9(7)	C(11)–C(12)–O(5)	108.8(6)
O(4)–C(12)–O(5)	123.3(7)	C(12)–O(5)–C(13)	116.1(6)
O(5)–C(13)–C(14)	110.3(6)	C(13)–C(14)–C(15)	119.6(8)
C(13)–C(14)–C(19)	121.2(8)	C(15)–C(14)–C(19)	119.1(8)
C(14)–C(15)–C(16)	119.8(10)	C(15)–C(16)–C(17)	120.4(10)
C(16)–C(17)–C(18)	119.3(9)	C(17)–C(18)–C(19)	120.5(9)
C(14)–C(19)–C(18)	120.8(8)		

TABLE 4. THE BEST PLANES

(a) Equation of the best planes

$X=ax+czcos\beta$, $Y=by$, $Z=czsin\beta$,

Plane I: O(1), C(5), O(2), N(1), C(6) $-0.9942X-0.0097Y-0.1067Z+13.450=0$

Plane II: C(6), C(10), O(3), N(2), C(11) $-0.4690X-0.0122Y+0.8831Z+4.255=0$

Plane III: C(11), C(12), O(4), O(5) $-0.4726X+0.8231Y-0.3147Z+2.809=0$

Plane IV: C(14), C(15), C(16), C(17), C(18), C(19) $-0.1932X-0.6808Y-0.7065Z+0.430=0$

Plane V: S, C(7), C(8), C(9), C(6) $-0.0582X+0.5285Y-0.8469Z+1.505=0$

(b) Dihedral angles (θ/°) between the planes

	I	II	III	IV
II	111.9			
III	119.7	93.8		
IV	105.9	121.7	104.3	
V	108.2	136.6	136.8	104.5

(c) Displacements($\times 10^3$d/Å) of atoms from the planes

The atoms with asterisks are not included in the best plane calculations.

O(1)	15	C(6)	10	C(11)	1	C(14)	−15	S	−42
C(5)	−12	C(10)	−9	C(12)	2	C(15)	15	C(6)	−21
O(2)	1	O(3)	0	O(4)	−1	C(16)	−3	C(7)	73
N(1)	−17	N(2)	−12	O(5)	−1	C(17)	−2	C(8)	−15
C(6)	15	C(11)	11	N(2)*	−559	C(18)	10	C(9)	10
C(2)*	17	H(19)*	−171	C(13)*	109	C(19)	−10		
C(4)*	20					C(13)*	7		
H(10)*	−284					H(24)*	−23		
						H(25)*	30		
						H(26)*	118		
						H(27)*	170		
						H(28)*	−115		

Table 5. The bond lengths (l/Å) and angles (ϕ/°) in the derivatives of methionine

	C^{α}–C^{β}	C^{β}–C^{γ}	C^{γ}–S^{δ}	S^{δ}–C^{ε}	C^{α}–C^{β}–C^{γ}	C^{β}–C^{γ}–S^{δ}	C^{γ}–S^{δ}–C^{ε}	Ref.
Ac-L-Met-OMe	1.538(6)	1.516(6)	1.800(5)	1.760(7)	113.0(3)	109.8(3)	102.0(3)	14
D,L-Ala-L,D-Met	1.526(4)	1.508(5)	1.811(4)	1.792(7)	113.9(3)	110.0(2)	99.1(2)	15
L-Met-L-Met(first)	1.531(4)	1.515(5)	1.816(3)	1.803(5)	112.7(3)	108.7(2)	99.8(2)	16
L-Met-L-Met(second)	1.543(4)	1.523(4)	1.813(3)	1.794(6)	112.2(2)	113.4(2)	99.9(2)	16
L-Met·HCl	1.532(7)	1.510(8)	1.818(8)	1.787(6)	113.8(8)	113.4(6)	101.3(6)	17
Boc-L-Met-Gly-OBz	1.539(8)	1.515(9)	1.795(7)	1.765(8)	111.3(5)	110.9(5)	101.1(4)	a
Average	1.535(6)	1.515(5)	1.809(9)	1.784(17)	112.8(10)	111.1(19)	100.4(12)	

a) This study.

Table 6. The torsion angles in the derivatives of methionine[a)]

	(χ^1/°)	(χ^2/°)	(χ^3/°)	Ref.
D,L-Met(α-form)	−60	177	81	12
D,L-Met(β-form)	−61	−176	−170	12
L-Met(molecule A)	−166.0	174.2	179.7	13
L-Met(molecule B)	−165.6	73.6	73.6	13
Ac-L-Met-OMe	−63.6	177.5	−178.6	14
D,L-Ala-L,D-Met	67.3	175.0	−173.8	15
L-Met-L-Met(first)	−167.2	−168.3	178.4	16
L-Met-L-Met(second)	68.0	−170.5	−57.6	16
L-Met·HCl	61	−178	69	17
Boc-L-Met-Gly-OBz	−73.2	175.3	174.9	b

a) All the torsion angles for the L-isomers are listed. b) This study.

around C(4), O(1), and C(5) are found, which are common in the Boc group.[11)]

The bond lengths and angles of the methionyl residue in several derivatives are compared in Table 5. The average bond lengths of C^{α}–C^{β} and C^{β}–C^{γ} of the methionyl residues are 1.535(6) and 1.515(5) Å, respectively. The corresponding bond lengths in the present peptide, 1.539(8) and 1.515(9) Å, are consistent to the average values. Thus in the side chain of the methionyl residue, the C^{α}–C^{β} bond is longer than the C^{β}–C^{γ} bond. As shown in Table 5, the C^{α}–C^{β}–C^{γ} angle is usually larger than the C^{β}–C^{γ}–S^{δ} angle, except for L-Met-L-Met (second).[16)] The C^{γ}–S^{δ}–C^{ε} angle of 101.1(4)° in the present peptide is close to the average of 100.4(1.2)°.

The torsion angles of the side chain of the methionyl residue are listed in Table 6, together with those of some methionine derivatives. The methionyl side chain, together with C′(=C(10)), has the most stable trans zig-zag conformation. The torsion angles of the side chain in the present peptide, χ^1=−73.2, χ^2=175.3, and χ^3=174.9°, coincide roughly with those of D,L-Met (β-form)[12)] and Ac-L-Met-OMe.[14)] In Table 6, the χ^1 values distribute uniformely in the values near −60, 180, and 60°. The present peptide takes χ^1 of −60°, which is favored as C^{γ} is between N and H. The χ^2 angle is around 180°, except for L-Met (molecule B),[13)] and it seems that the χ^3 angle tends to be predominantly near 180°.

The parallel β-sheet structure extended along the b axis is seen in the crystal, as shown in Fig. 3. The main chain torsion angles (ϕ,ψ) of the methionyl residue (−110.6, 108.3°) are close to those, (−119, 113°), of the parallel β-pleated sheet structure.[18)] The ten-membered

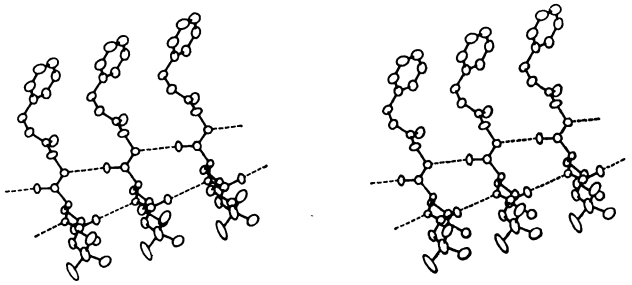

Fig. 3. Packing scheme viewed along the a axis (stereoscopic view). The parallel β-pleated sheet structure is formed. Hydrogen bonds are drawn as dotted lines.

ring hydrogen bonding pattern is formed from one molecule to the next molecule translated along the b axis. The geometries of the hydrogen bonds are: N(1)···O(2) 2.961 Å, H···O(2) 2.44 Å, ∠N(1)–H···O(2) 145°; N(2)···O(3) 2.897 Å, H···O(3) 2.19 Å, ∠N(2)–H···O(3) 159°.

The parallel β-structure is found in several other oligopeptides. Their torsion angles (ϕ,ψ) are; (−126, 132°) in Gly-L-Phe-Gly,[19)] (−102, 106°) in Br-Ac-L-Phe-L-Phe-OEt,[20)] (−100, 110°) in Cl-Ac-L-Phe-L-Phe-OEt,[20)] (−124, 103°) in Boc-(S-benzoyl)-L-Cys-Gly-OMe,[21)] (−106, 108°) in Ac-D,L-Phe-NMe,[22)] and (−107, 104°) in Ac-L-Phe-NMe.[23)]

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