N-(*tert*-Butoxycarbonyl)-L-valyl-L-valine methyl ester: a twisted, parallel β-sheet in the crystal structure of a protected dipeptide

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SUPPLEMENTARY MATERIAL

Table 1s
Important torsion angles (°) in the crystal structures of X-OOC-Xaa_1-Xaa_2-OY protected dipeptides in the Cambridge Structural Database (Allen, 2002).

Table 2s
Structures of acyclic peptides with parallel β-sheets in the Cambridge Structural Database (Allen, 2002).

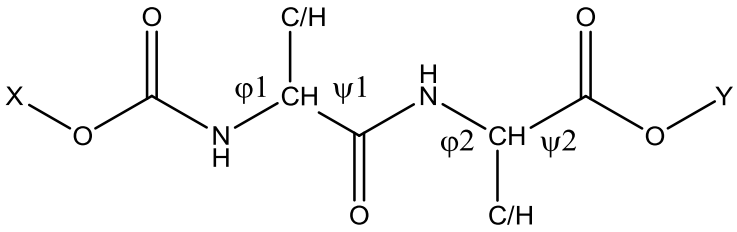
Fig. 1S. Parallel β-sheet in the structure of the tripeptide *N*-Boc-L-Tyr-L-Val-L-Tyr-OMe (CSD refcode DALREO; Ray *et al*. 2004). In Figs. 1S – 3S amino acid side chains as well as N- and C-terminal blocking groups have been removed for clarity.

Fig. 2S. Parallel β-sheet in the structure of the pentapeptide *N*-Boc-L-Phe-L-Ala-L-Ile-ΔPhe-L-Ala-OMe where ΔPhe is α,β−didehydro-Phe (COGKAL; Gupta *et al*., 2008).

References
Allen, F. H. (2002). *Acta Cryst*. B**58**, 380-388.
Gupta, M., Acharya, R., Mishra, A., Ramakumar, S., Ahmed, F., Chauhan, V. S. (2008). *ChemBioChem* **9**, 1375-1378.
Ray, S., Haldar, D., Drew, M. G. B., Banerjee, A. (2004). *Org. Lett*. **6**, 4463-4465.

Table 1s

Important torsion angles (°) in the crystal structures of X-OOC-Xaa$_1$-Xaa$_2$-OY protected dipeptides in the CSD (Allen 2002), where Xaa is an amino acid involved in acyclic bonds only. Pairs of phi and psi torsion angles substantially deviating from those observed in the present work have been highlighted in a grey tone.



Refcode	Xaa-Xaa[a]	phi1	psi1	phi2	psi2	X[b]	Y[b]	arom[c]
This work	L-Val-L-Val	-87.6	126.2	-62.6	149.1	tBu	Me	
This work	L-Val-L-Val	-117.6	134.3	-57.0	141.6	tBu	Me	
This work	L-Val-L-Val	-76.2	129.5	-58.3	145.5	tBu	Me	
BCMEGL	L-Met-Gly	-110.8	108.4	-76.5	155.3	tBu	Bz	x
BIVLIB	L-Phe-L-Phe	-131.4	102.3	-156.1	169.9	tBu	Bz	x
BUSCGL	*S*-Bz-L-Cys-Gly	-124.1	103.2	152.7	170.4	tBu	Me	x
CIHLAG	other[d]	152.0	-128.5	160.8	179.5	tBu	Bz	x
DENNUF	L-Met-Gly	-118.9	115.4	-54.3	-39.4	tBu	Et	
ELIJOY	L-Leu-L-Ala	-125.1	129.8	-62.0	154.4	tBu	Et	
ELIJOY	L-Leu-L-Ala	-65.8	155.0	-57.3	138.4	tBu	Et	
ELIJOY	L-Leu-L-Ala	-104.7	142.1	-74.9	158.2	tBu	Et	
GUFKEX	L-Phe-Leu	-106.3	116.6	-73.3	157.6	tBu	Bz	x
GUFKEX	L-Phe-Leu	-122.3	112.0	-64.6	-16.7	tBu	Bz	x
GUFKEX	L-Phe-Leu	-70.1	142.2	-103.9	-58.9	tBu	Bz	x
GUFKEX	L-Phe-Leu	-118.2	146.9	-120.2	37.2	tBu	Bz	x
GUFKEX	L-Phe-Leu	-125.9	128.3	-97.5	17.9	tBu	Bz	x
GUFKEX	L-Phe-Leu	-70.3	139.7	-81.1	-171.6	tBu	Bz	x
GUFKEX	L-Phe-Leu	-117.0	127.8	-59.6	-49.8	tBu	Bz	x
IDOFOX	L-Leu-L-Val	-96.9	128.6	-63.9	155.0	tBu	CH_2CCl_3	
IWUCUY	L-Ala-L-Leu	-75.7	-32.6	-101.6	142.0	tBu	L-Lac	
JAYWUC	L-Leu-L-Ala	-91.5	130.6	-61.6	151.8	tBu	CH_2CCl_3	
LANQOH	L-t-Leu-Gly	-128.1	136.7	-148.7	177.0	Bz	tBu	x
LANQOH	L-t-Leu-Gly	-132.2	134.2	-147.9	-178.7	Bz	tBu	x
MUDXIS	other[e]	-125.9	150.8	-82.7	7.4	Bz	Me	x
PATWEN	L-Val-L-Phe	-96.4	101.4	-124.0	34.0	tBu	Me	x
PIYSAS	L-Leu-L-Leu	-112.2	120.4	-66.9	145.7	tBu	L-Lac-OEt	
PIYSAS	L-Leu-L-Leu	-67.5	128.0	-78.4	158.3	tBu	L-Lac-OEt	
SAGTUQ	L-Tyr-Gly	-122.4	-28.4	-84.4	180.0	Bz	Et	x
XAHWOT	L-Ile-L-Leu	-104.5	134.1	-63.0	148.4	tBu	Me	
YULWOS	other[f]	-66.8	131.9	-104.4	164.4	tBu	tBu	
YULWOS	other[f]	-130.5	137.8	-124.6	164.8	tBu	tBu	
ZIGCIB	L-Ala-*S*-Bz-L-Cys	-130.1	129.3	-148.3	174.8	tBu	Me	x

[a] *S*-Bz-L-Cys = *S*-benzyl-L-Cys, L-t-Leu = *tert*-butyl-L-Leu. [b] tBu = *tert*-butyl, Bz = benzyl, Me = methyl, Et = ethyl, L-Lac = L-lactic acid, L-Lac-OEt = L-lactic acid ethyl ester. [c] Peptides indicated with x have at least one aromatic moiety in the protecting groups or the side chains. [d] α-*tert*-Butyl-*N*-(*N*-*tert*-butoxycarbonyl-*O*^{5}-benzyl-α-L-glutamyl)-*O*^{5}-benzyl-L-glutamate. [e] Methyl 2-(((1-((benzoxycarbonyl)amino)-1-benzylmethyl)carbonyl)amino)-2-(2-oxocyclohexyl)ethanoate. [f] *tert*-Butyl -*N*-(2-((*tert*-butoxycarbonyl)amino)-4-(chloromethyl)-3-methylhex-4-enoyl)leucinate.

Table 2s

Structures of acyclic peptides with parallel β-sheets in the Cambridge Structural Database

Refcode	Space group	*Z*'	N_{res}[a]	Comment
Flat tapes				
ADOFAB	$P2_1$	1	2	
BAJPIM	$P2_12_12_1$	1	4	H bond statistical outlier
BCMEGL	$P2_1$	1	2	
BIPHOX10	$P2_12_12_1$	1	4	
BIVLIB	$P2_1$	1	2	
BUSCGL	$P2_1$	1	2	
CEPQIY	$P2_12_12_1$	1	2	
CEPQOE	$P2_12_12_1$	1	2	
CEPQUK	$P2_1$	1	2	
COGKAL	$P2_1$	1	5	
COPBIS10	$C2$	1	2	
DALREO	$C2$	1	3	
DALRIS	$C2$	1	3	
DENNUF	$P2_1$	1	2	
FAFSUA	$P2_1$	1	2	
FAVLOD	$P2_12_12_1$	1	3	
FUMJUT	$C2$	1	2	
FUJDET	$P2_1$	1	2	
GEMDEH	$P2_12_12_1$	1	2	
GPAGLM	$P2_12_12_1$	1	3	
HICNEM	$C2$	1	2	
HURDAZ	$P4_32_12$	1	2	
JECYUL	$P1$	1	4	
JOVWEW	$P2_1$	1	4	
KAXMIG	$C2$	0.5	2	disulfide bridge
KEHXEB	$P2_1$	1	3	
KEHXIF	$P2_1$	1	3	
KEHXOL	$P1$	1	3	
KEHXUR	$P2$	2	3	
LECDIH	$P2_1/n$	1	4	
LPTILL	$P2_1$	1	4	H bond statistical outlier
OCAWEV	$P2_12_12_1$	1	2	
PATFAR	$P2_12_12_1$	1	3	
PATWEN	$P2_12_12_1$	1	2	
QOWREZ	$P2_12_12_1$	1	10	hairpin, two β-Phe residues and one D-Pro
RUHWOH	$P2_1$	1	2	H bond statistical outlier
RUYLUS	$C2/c$	2	2	achiral (Gly residues)
SAMGAP	$P2_1$	1	2	
SEMQUX	$P2_1$	1	3	one γ-aminobutyryl residue
SEMRAE	$P2_1$	1	3	one γ-aminobutyryl residue
SEMREI	$P2_12_12_1$	1	3	one γ-aminobutyryl residue
UCIHEU	$C2$	0.5	2	
VAXROC	$P1$	1	2	
VISKUE	$P2_1$	1	2	
WISGAG	$P2_1$	1	2	
XIMQIU	$P2_12_12_1$	1	2	

YAQBOH	$P2_1$	1	2	
ZIGCIB	$P2_12_12_1$	1	2	
ZZZIFQ01	$P2_1$	2	3	H bond statistical outlier
Helices				
Repeating unit 8				
PIYSAS	$P4_32_12$	2	2	
Repeating unit 7				
GUFKEX	$P2_1$	7	2	
Repeating unit 6				
BIMGAF10	$P6_5$	1	2	
GUFWEJ	$P2_12_12_1$	3	2	
IDOFOX	$P6_5$	1	2	
JAYWUC	$P6_5$	1	2	
JEQKAS	$P6_5$	1	2	
REVJAE	$P6_5$	1	2	
RUHWIB	$P6_5$	1	2	
WEVCUW	$P6_5$	1	2	amide H atoms misplaced[b]
XAHWOT	$P6_5$	1	2	
YULVOS	$P3_2$	2	2	
ZADJAP	$P6_1$	1	2	unusual 2-methylVal residue
Repeating unit 4				
BLEGLE	$P2_1$/n	2	2	racemate
ERIMAT	$P2_1$	2	2	disulfide bridge
FABLUP10	$I4_1$	1	2	
IGOLOF	$P4_3$	1	2	
LERHUM	$P4_3$	4	2	only one tape with parallel chains
MAKLEQ	$P4_3$	1	2	
XEZDUC	$I4_1$/a	1	2	achiral

[a] Number of residues in the peptide.
[b] Tetrahedral arrangement of H atoms at amide N atoms, entry not included in H bond statistics.

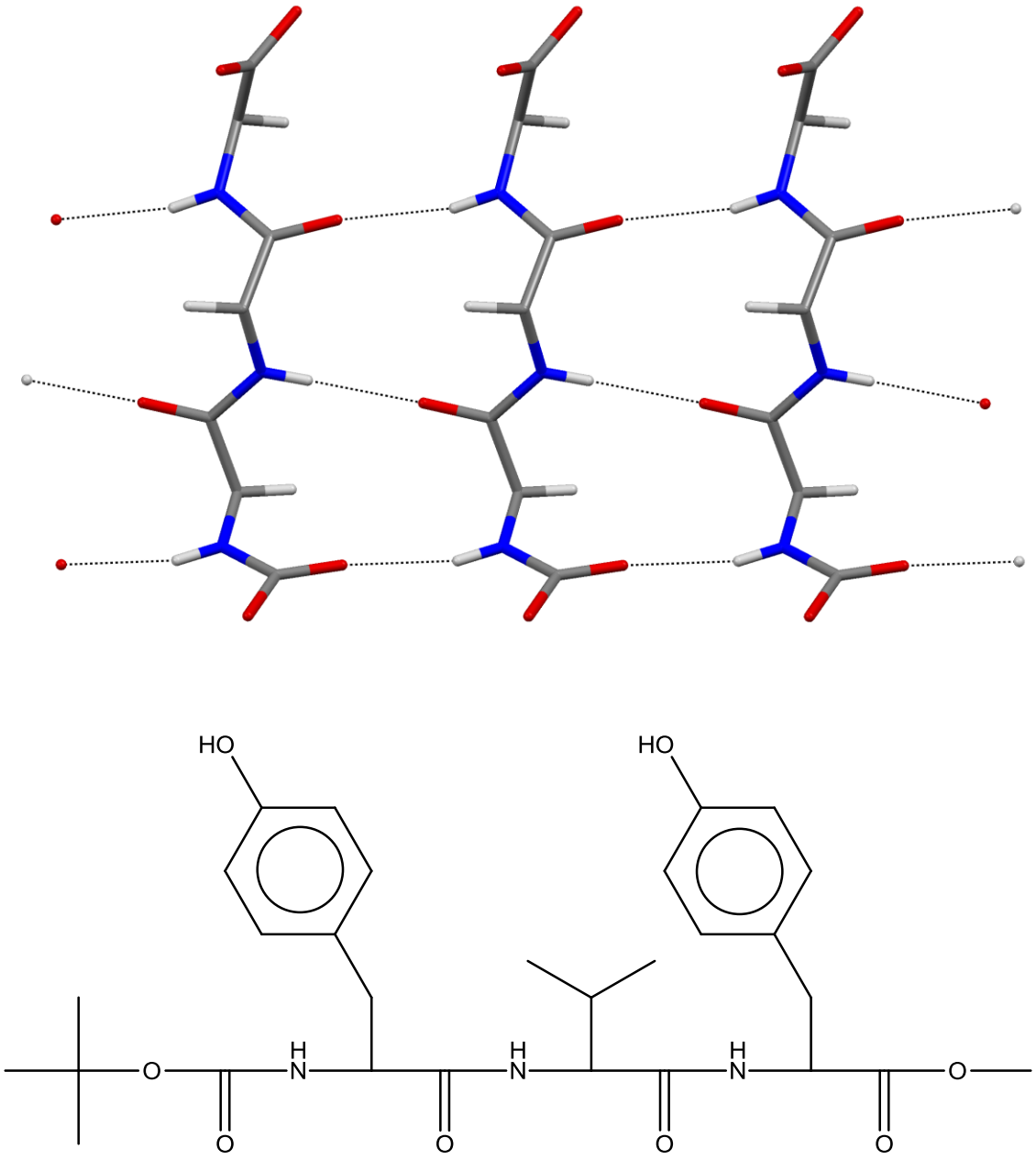


Fig. 1S

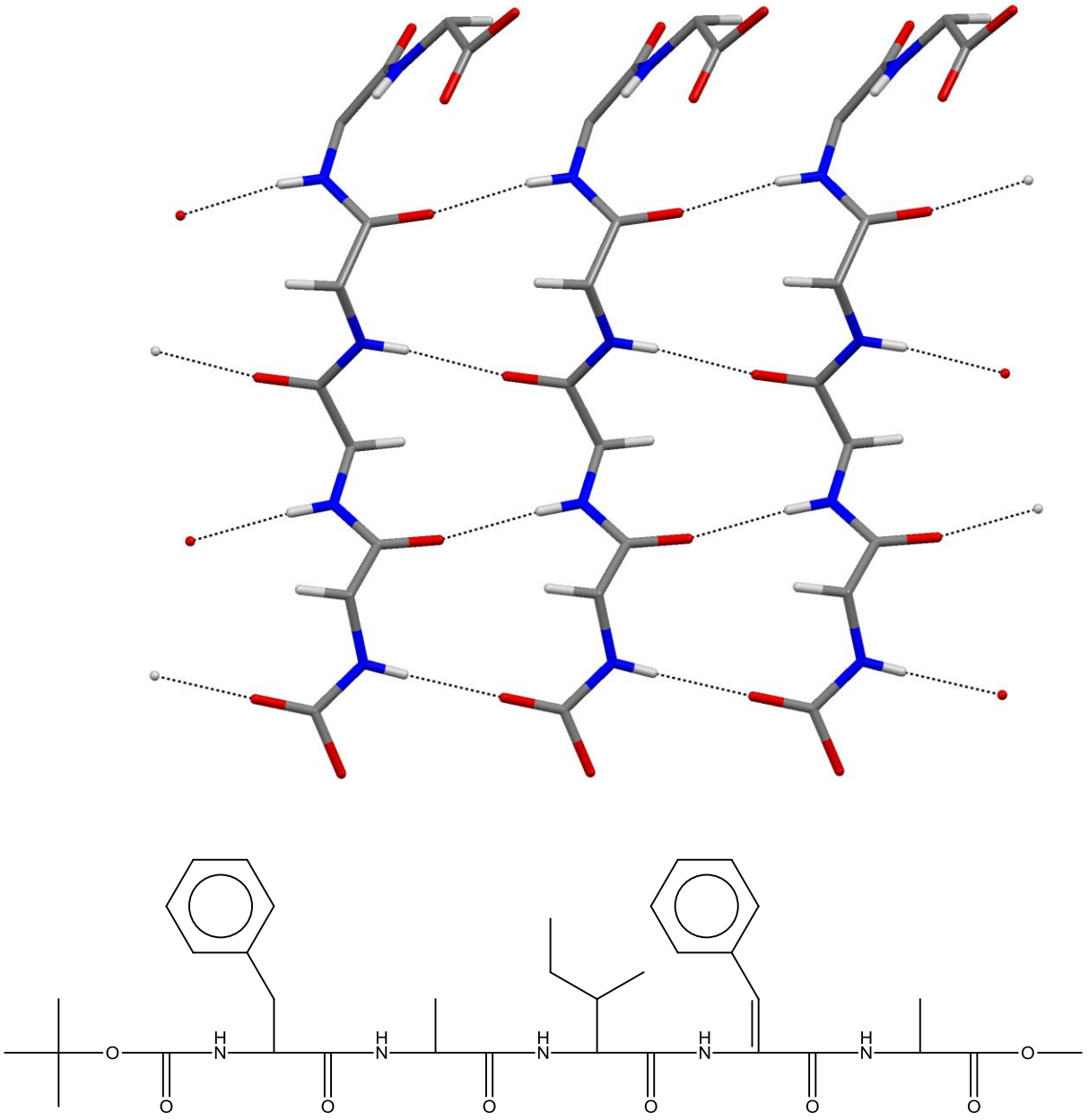


Fig. 2S