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Supporting Information

The Chirality Chain in Valine: How the Configuration at the C_α Position through the $O_{cis}C'C_\alpha N$ Torsional System Leads to Distortion of the Planar Group $C_\alpha C'(O_{cis})O_{trans}$ to a Flat Tetrahedron

Henri Brunner*[a] and Takashi Tsuno*[b]

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Table S1. Zwitterionic valine structures, including all the structure determinations of the valine racemates and enantiomers

Entry	CSD symbol[a]	Chirality chain			Distanses		Bond angles		Comments
		Config. C_α	O_{cis}-C'-C_α-N rotation angle ψ / º	O_{trans}-C'-C_α-O_{cis} pyramidal angle θ / º	O_{cis}-N / Å	O_{cis}-C(^{i}Pr) / Å	N-C_α-C'(O) / º	(^{i}Pr)C-C_α-C'(O) / º	
1	LVALIN01(1)	L	-17.48	-177.78	2.66	3.39	109.26	112.72	enantiomer(1)
2	LVALIN05(1)	L	-18.78	-177.00	2.65	3.37	109.12	113.22	enantiomer(1)
3	LVALIN(1)	L	-19.46	-177.51	2.65	3.38	109.55	113.74	enantiomer(1)
4	VALIDL03	L	-23.31	-179.09	2.67	3.33	110.02	112.47	racemate[b]
5	VALIDL02	L	-23.48	-179.09	2.67	3.33	109.49	112.53	racemate[b]
6	VALIDL	L	-24.21	-179.78	2.67	3.33	109.08	112.96	racemate[b]
7	OXEMEL	L	-24.63	-178.47	2.67	3.32	109.28	111.29	enantiomer
8	LVALIN01(2)	L	-42.81	-177.66	2.76	3.10	109.33	110.48	enantiomer(2)
9	LVALIN(2)	L	-43.79	-178.36	2.77	3.06	109.14	109.24	enantiomer(2)
10	LVALIN05(2)	L	-43.88	-177.52	2.76	3.09	108.88	111.01	enantiomer(2)
11	AHEJEC01(1)[c]	D	17.55	177.91	2.66	3.38	109.36	112.76	enantiomer(1)
12	AHEJEC(1)[c]	D	17.95	177.75	2.66	3.38	109.31	112.98	enantiomer(1)
13	AHEJEC02(1)[c]	D	18.09	177.88	2.66	3.38	109.41	113.08	enantiomer(1)
14	AHEJEC03(1)[c]	D	18.36	177.82	2.66	3.38	109.34	113.03	enantiomer(1)
15	AHEJEC01(2)[c]	D	43.28	177.20	2.76	3.09	109.19	110.60	enantiomer(2)
16	AHEJEC(2)[c]	D	43.55	177.22	2.75	3.09	109.09	110.59	enantiomer(2)
17	AHEJEC02(2)[c]	D	43.80	177.12	2.75	3.09	109.11	109.91	enantiomer(2)
18	AHEJEC03(2)[c]	D	43.99	177.10	2.75	3.09	109.23	110.74	enantiomer(2)
19	QOQWEY[1]	L	3.49	-182.28	2.61	3.51	108.07	111.73	+ L-valine·$HClO_4$ adduct
20	OPEFUL[1]	L	-5.53	-181.00	2.60	3.51	107.19	116.10	+ L-valine·HCl adduct
21	HAGYEU	L	-10.60	-179.86	2.64	3.60	109.75	111.46	+ fumaric acid
22	EWOZIZ	L	-10.68	-180.04	2.63	3.42	109.56	111.11	+ fumaric acid
23	OCOLID[1]	L	-10.76	-179.37	2.61	3.50	106.74	118.21	+ valine·HBr adduct
24	GUQJUZ[1](1)	L	-12.95	-180.76	2.64	3.40	109.35	111.53	+ valine·naphthalene-1,5-$(SO_3H)_2$ adduct
25	GUQJUZ[1](2)	L	-20.39	-177.28	2.64	3.30	107.90	112.64	+ valine·naphthalene-1,5-$(SO_3H)_2$ adduct
26	GALPIT	L	-24.03	-178.61	2.67	3.33	109.69	112.73	+ (*R*)-PhOCHMe-COOH
27	VIKLUX	L	-24.91	-178.69	2.68	3.32	109.39	110.96	+ fumaric acid
28	DUMPEI(1)	L	-31.03	-178.36	2.62	3.27	104.91	109.36	+ calix[4]resorcinarene, CF_3CH_2OH
29	PAHCIL[1]	L	-32.33	-179.19	2.67	3.26	107.73	114.36	+ valine·trinitrophenol adduct
30	GOLVUY	L	-35.59	-177.34	2.69	3.17	108.04	110.44	+ D-n-BuAA[d]
31	BERQIY	L	-36.05	-177.54	2.70	3.17	107.97	110.68	+ D-methionine
32	BERQEU	L	-36.55	-177.49	2.70	3.16	108.14	110.42	+ D-n-PrAA[d]
33	BERQAQ	L	-37.47	-177.47	2.70	3.15	107.91	110.39	+ D-EtAA[d]
34	LENGIX	L	-42.16	-178.37	2.76	3.10	109.52	110.23	+ L-isoleucine
35	ALIHUA	L	-42.72	-177.29	2.75	3.11	108.87	110.98	+ L-isoleucine
36	DUMPEI(2)	L	-43.65	-180.10	2.77	3.06	110.59	109.59	+ calix[4]resorcinarene, CF_3CH_2OH
37	OHAROF	L	-53.26	-171.38	2.77	3.17	107.55	116.32	+ Mn cluster
38	FITMEA[c]	D	23.91	179.25	2.68	3.34	109.40	112.69	+ L-isoleucine
39	BERPET[c]	D	24.08	179.27	2.67	3.33	109.32	110.05	+ L-leucine
40	SONCED[c]	D	25.84	179.48	2.68	3.31	109.52	112.63	+ L-phenylalanine
	Average		-27.74	-178.32	2.69	3.28	108.86	111.95	

[a]Parenthesis () indicate independent molecules in the unit cell, while brackets [] differentiate between $^+NH_3CH(^iPr)COO^-$ and $^+NH_3CH(^iPr)COOH$. [b]Racemates given as L-compounds. [c]For average calculation rotation angle and distortion angle inverted. [d]AA = amino acid.

Table S2. Valine zwitterions protonated at the carboxylic group by strong acids

Entry	CSD symbol[a]	Chirality chain			Distanses		Bond angles		Comments
		Config. C_α	O_{cis}-C'-C_α-N rotation angle ψ / º	O_{trans}-C'-C_α-O_{cis} pyramidal angle θ / º	O_{cis}-N / Å	O_{cis}-C(^{i}Pr) / Å	N-C_α-C'(O) / º	(^{i}Pr)C-C_α-C'(O) / º	
1	WIHQUA(1)	L	1.77	-182.10	2.66	3.50	107.24	111.77	H_2NbOF_5
2	BANPOW(1)	L	1.11	-180.32	2.66	3.55	106.84	113.00	$HClO_4$
3	BANPOW(2)[b]	L	-0.29	-179.96	2.65	3.53	106.44	113.14	$HClO_4$
4	NUZMIG	L	-0.74	-181.98	2.67	3.49	110.48	107.86	maleic acid
5	PAHCIL[2]	L	-1.53	-179.81	2.66	3.53	107.49	114.99	trinitrophenol
6	BANPOW(3)[b]	L	-2.10	-179.99	2.65	3.52	107.12	113.40	$HClO_4$
7	QOQWEY[2]	L	-1.79	-178.81	2.61	3.50	106.33	113.75	$HClO_4$, H_2O
8	VALHCL10	L	-3.72	-182.11	2.68	3.48	108.41	109.80	HCl, H_2O
9	VALHCL12	L	-6.11	-180.33	2.68	3.46	108.07	111.73	HCl, H_2O
10	VALHCL11	L	-6.13	-180.62	2.65	3.50	107.71	112.22	HCl, H_2O
11	OPEFUL[2]	L	-8.14	-181.54	2.65	3.58	107.02	115.20	HCl
12	GUQJUZ[2](1)	L	-8.86	-179.57	2.64	3.40	106.81	110.60	naphthalene-1,5-sulfonic acid, H_2O
13	XAXHAH(2)[b]	L	-9.89	-183.48	2.48	3.26	109.84	114.09	phospho-tungsten acid
14	VALEHC11	L	-11.15	-179.75	2.65	3.45	106.84	114.34	HCl
15	VALEHC10	L	-11.17	-178.65	2.64	3.46	106.23	114.51	HCl
16	TUZJIJ	L	-11.44	-177.98	2.65	3.42	107.86	110.89	TsOH, H_2O
17	LUDHAT	L	-11.50	-179.26	2.63	3.45	107.90	111.75	H_3PO_4
18	OCOLID[2]	L	-11.60	-179.81	2.63	3.45	106.69	115.42	HBr
19	HURXEX(1)	L	-11.68	-179.54	2.64	3.44	107.90	113.61	H_2PO_3
20	HURXEX(2)	L	-12.11	-179.99	2.66	3.46	107.88	114.45	H_2PO_3
21	GUQJUZ[2](2)	L	-13.31	-178.58	2.63	3.42	109.35	111.53	naphthalene-1,5-sulfonic acid, H_2O
22	QURSUR	L	-15.48	-178.68	2.65	3.40	106.46	111.39	maleic acid
23	QEMGIZ	L	-15.54	-178.85	2.66	3.40	107.16	113.08	CF_3COOH
24	WIHQUA(2)[b]	L	-15.68	-178.90	2.68	3.42	107.69	113.46	H_2NbOF_5
25	RAJKUK	L	-15.83	-179.68	2.68	3.40	107.27	112.64	HCl, Me ester
26	RUXWIQ(1)	L	-16.49	-177.96	2.65	3.35	106.76	110.87	H_2SeO_4, H_2O
27	DLVALC	L	-16.82	-180.16	2.68	3.42	106.72	114.26	HCl
28	RUXWIQ(2)	L	-16.99	-179.64	2.67	3.36	107.69	110.21	H_2SeO_4, H_2O
29	XAXHAH(1)	L	-19.57	-175.92	2.81	3.46	104.06	110.63	phospho-tungsten acid
30	VALNIT01(1)	L	-19.96	-178.99	2.69	3.38	107.59	113.19	HNO_3
31	ROKBOI02(1)	L	-20.32	-179.24	2.70	3.39	107.91	111.38	HNO_3
32	BANPOW(4)	L	-20.98	-177.94	2.69	3.34	107.69	110.13	$HClO_4$
33	FACXUD	L	-22.42	-178.99	2.68	3.34	107.11	112.46	CF_3COOH
34	VALNIT01(2)	L	-22.67	-178.80	2.70	3.37	106.97	113.87	HNO_3
35	UHEPIG	L	-23.48	-178.82	2.68	3.34	107.12	113.85	$HPO(Onp)_2$, H_2O
36	HOTXIY	L	-23.81	-177.94	2.71	3.31	109.07	111.44	RCOOH
37	BEZNUR	L	-23.83	-177.21	2.68	3.31	106.79	111.06	H_2SiF_6
38	ROKBOI01(1)	L	-23.83	-179.57	2.71	3.33	108.40	113.26	HNO_3
39	WAPQOV	L	-24.91	-178.38	2.74	3.35	108.10	112.62	cinnamic acid, Me ester
40	DUMZOB	L	-25.00	-179.10	2.71	3.33	107.07	113.47	HCl, Bn ester
41	RUXWIQ(3)	L	-25.07	-178.27	2.71	3.32	107.36	111.61	H_2SeO_4
42	ROKBOI(1)	L	-25.24	-178.57	2.72	3.32	107.34	113.67	HNO_3
43	RUXWIQ(4)	L	-25.96	-176.98	2.69	3.31	107.21	112.75	H_2SeO_4
44	ROKBOI02(2)	L	-27.96	-178.36	2.77	3.30	109.13	110.18	HNO_3
45	ABEHOF	L	-28.23	-178.61	2.69	3.26	107.63	112.06	trinitrophenol
46	WAPQIP	L	-30.67	-181.32	2.74	3.32	107.59	113.31	4-MeC_6H_4-CH=CH-OOH, $CHCl_3$, Me ester
47	ROKBOI01(2)	L	-31.78	-180.23	2.76	3.24	109.14	113.41	HNO_3
48	ROKBOI(2)	L	-32.49	-179.22	2.76	3.24	108.63	109.72	HNO_3
49	VALNIT01(3)[b]	L	-32.62	-178.57	2.73	3.21	107.59	110.14	HNO_3
50	VALNIT01(4)[b]	L	-33.03	-178.47	2.72	3.22	106.88	110.81	HNO_3
51	ROKBOI02(3)	L	-33.74	-178.21	2.74	3.22	107.70	110.95	HNO_3
52	ROKBOI02(4)	L	-43.91	-176.89	2.82	3.10	108.74	108.98	HNO_3
53	HABXAK[c]	D	17.65	179.59	2.67	3.02	107.20	113.32	HCl, Me ester
54	HOSMAE[c]	D	20.90	176.81	2.62	3.32	110.37	111.01	RCOOH
Valine zwitterions coordinated in complexes									
55	ESAPET(1)	L	-12.29	-182.91	2.64	3.41	110.43	114.18	H_2PbO_3, $2HNO_3$, H_2O
56	ESAPET01(1)	L	-14.91	-179.54	2.65	3.40	110.26	112.59	H_2PbO_3, $2HNO_3$, H_2O
57	ACETUX	L	-19.43	-181.01	2.55	3.30	107.94	112.27	$ZnCl_2$
58	OHAROF[b]	L	-23.53	-176.46	2.57	3.31	107.28	113.48	Mn cluster
59	DIZXUH(1)	L	-23.69	-178.69	2.52	3.30	107.18	114.50	$FeBr_2$
60	ESAPET02(1)	L	-27.29	-171.61	2.69	3.29	108.64	115.03	H_2PbO_3, $2HNO_3$, H_2O
61	ESAPET01(2)	L	-29.13	-177.97	2.69	3.28	107.10	111.90	H_2PbO_3, $2HNO_3$, H_2O
62	ESAPET02(2)	L	-29.14	-177.24	2.70	3.27	108.35	111.28	H_2PbO_3,

									$2HNO_3$, H_2O
63	ESAPET(2)	L	-32.97	-175.39	2.69	3.28	108.91	113.31	H_2PbO_3, $2HNO_3$, H_2O
64	DIZXUH(2)	L	-33.48	-178.95	2.56	3.17	107.43	112.55	$FeBr_2$
65	VALCAC[b]	L	-35.46	-179.94	2.67	3.17	105.99	110.48	$CaCl_2(H_2O)$
	Average		-18.69	-179.06	2.67	3.36	107.69	112.38	

[a]Parenthesis () indicate independent molecules in the unit cell, while brackets [] differentiate between $^+NH_3CH(^iPr)COO^-$ and $^+NH_3CH(^iPr)COOH$. [b]Racemates given as L-compounds. [c]For average calculation rotation angle and distortion angle inverted.

Table S3. Dipeptides with valine at carboxy and amino end

Entry	CSD symbol[a]	Dipeptide	Chirality chain			Distanses		Bond angles	
			Config. C_α	O_{cis}-C'-C_α-N rotation angle ψ / º	$O_{trasn}(N_{amide})$-C'-C_α-O_{cis} pyramidal angle θ / º	O_{cis}-N / Å	O_{cis}-C(^{i}Pr) / Å	N-C_α-C'(O) / º	(^{i}Pr)C-C_α-C'(O) / º
Valine at carboxy end									
1	FOBXAW(1)	Asn-Val	L	6.45	-180.79	2.67	3.58	112.54	111.67
2	XUDWAU(1)	Ala-Val	L	-3.09	-202.39	2.72	3.47	107.75	115.50
3	LACCAT	Trp-Val	L	-8.88	-179.77	2.65	3.44	110.19	111.46
4	NAFZID(1)	Leu-Val	L	-14.30	-178.35	2.73	3.40	109.41	111.06
5	TIPTUH	Glu-Val	L	-14.56	-180.14	2.70	3.42	111.21	112.49
6	XUDWAU(2)	Ala-Val	L	-16.59	-180.05	2.72	3.39	110.37	111.01
7	EFUCIS	Ala-Val	L	-19.20	-187.39	2.62	3.43	114.11	115.91
8	NAFZID(2)	Leu-Val	L	-24.39	-178.51	2.70	3.35	112.71	111.15
9	BIBVOX	Pro-Val	L	-24.39	-180.91	2.74	3.32	112.60	106.11
10	EYIVAJ(1)	Ser-Val	L	-24.66	-180.27	2.70	3.34	112.93	108.81
11	HEGMAI	Ile-Val	L	-25.15	-177.08	2.77	3.29	109.38	111.56
12	AQASAM	Ile-Val	L	-25.33	-176.87	2.76	3.31	109.95	111.46
13	AQASIU	Val-Val	L	-26.09	-177.57	2.76	3.29	109.46	111.49
14	HEGLUB	Val-Val	L	-26.26	-177.41	2.74	3.28	109.69	112.02
15	WEVWOK(2)	Gly-Val	L	-26.28	-178.91	2.71	3.31	112.47	109.47
16	WEVWOK(5)	Gly-Val	L	-27.45	-179.88	2.72	3.30	112.89	108.77
17	SEYWAU	Lys-Val HCl	L	-27.69	-180.56	2.70	3.26	110.43	108.25
18	SEGYOS	Arg-Val	L	-28.86	-177.47	2.70	3.28	111.62	113.35
19	WEVWOK(6)	Gly-Val	L	-29.28	-178.82	2.70	3.26	111.75	109.40
20	WEVWOK(1)	Gly-Val	L	-30.50	-179.78	2.73	3.26	112.46	108.75
21	WEVWOK(3)	Gly-Val	L	-31.27	-177.16	2.69	3.24	112.41	109.05
22	NAFZID(3)	Leu-Val	L	-32.84	-181.45	2.67	3.32	114.75	111.18
23	XUDVOH04	Ala-Val	L	-34.93	-176.51	2.74	3.21	110.97	110.82
24	WEVWOK(4)	Gly-Val	L	-35.84	-177.59	2.72	3.19	111.75	108.99
25	WEVWOK(7)	Gly-Val	L	-35.87	-178.08	2.70	3.16	110.53	109.58
26	XUDVOH01	Ala-Val	L	-36.81	-175.68	2.75	3.21	111.91	111.91
27	XUDWAU(3)	Ala-Val	L	-39.07	-179.74	2.75	3.18	110.49	110.64
28	FOBXAW(2)	Asn-Val	L	-41.54	-178.15	2.84	3.21	111.85	110.43
29	BEQJEN	Try-Val	L	-42.70	-177.43	2.82	3.15	111.21	111.22
30	EPATUM	Ala-Val	L	-42.80	-173.89	2.76	3.13	110.86	111.32
31	XUDVUN	Ala-Val	L	-42.82	-179.96	2.77	3.11	109.43	111.46
32	XUDWAU(4)	Ala-Val	L	-44.30	-179.35	2.77	3.07	108.32	111.11
33	XUDVOH	Ala-Val	L	-44.60	-176.43	2.77	3.11	110.50	111.26
34	XUDVIB	Ala-Val	L	-45.23	-176.33	2.76	3.09	110.40	111.34
35	CIHNUC	Tyr-Val	L	-45.49	-177.97	2.82	3.11	109.91	110.37
36	NAFZID(4)	Leu-Val	L	-46.51	-177.28	2.79	3.08	110.18	110.32
37	XUDVOH05	Ala-Val	L	-48.25	-174.91	2.78	3.07	111.45	111.27
38	FOBXAW(3)	Asn-Val	L	-48.89	-178.64	2.76	3.08	111.59	111.08
39	SUWLOL(3)	Leu-Val	L	-54.26	-179.77	2.81	3.01	110.76	109.20
40	SUWLOL(1)	Leu-Val	L	-54.83	-179.63	2.81	3.02	111.44	109.83
41	SUWLOL(4)	Leu-Val	L	-55.25	-178.05	2.90	3.08	111.77	110.41
42	SUWLOL(2)	Leu-Val	L	-56.09	-178.60	2.91	3.09	112.22	111.14
43	SUWLIF	Leu-Val	L	-64.79	-180.65	2.88	2.95	112.04	110.51
44	JUCSEF01	Leu-Val	L	-71.60	-184.02	3.02	2.86	108.95	110.51
Valine at amino end									
45	MOBYEH(1)[b]	Val-Phe	L	135.42[c]	-175.49[c]	-	-	109.71	111.41
46	MOBYEH(2)[b]	Val-Phe	L	133.22[c]	-177.17[c]	-	-	109.89	111.68
47	MOBYEH(3)[b]	Val-Phe	L	130.25[c]	-177.58[c]	-	-	110.14	112.11
48	MOBYEH(4)[b]	Val-Phe	L	125.42[c]	-177.57[c]	-	-	109.61	110.71
49	NAYZET(1)	Val-Ala	L	-10.91	-178.03	2.61	3.44	106.50	112.19
50	AQASEQ	Val-Ile	L	-13.58	-180.89	2.59	3.44	105.03	113.04
51	AQASIU	Val-Val	L	-13.83	-180.11	2.59	3.45	105.46	113.97
52	HEGMEM01	Val-Ile	L	-14.44	-180.24	2.60	3.43	105.78	113.42
53	HEGMEM	Val-Ile	L	-14.97	-179.98	2.59	3.44	105.67	114.19
54	HEGLUB	Val-Val	L	-15.11	-179.73	2.74	3.28	105.46	113.81
55	WIRYEB02	Val-Ala	L	-16.55	-178.42	2.59	3.38	105.60	113.02
56	WIRYEB	Val-Ala	L	-17.10	-180.00	2.59	3.37	105.99	112.55
57	NAYZET(2)	Val-Ala	L	-18.17	-178.31	2.64	3.38	107.08	111.58
58	NAYZIX	Val-Ala	L	-18.85	-178.32	2.59	3.37	105.40	112.70
59	CAZGOA(1)	Val-Ser	L	-19.65	-179.47	2.58	3.37	105.38	113.44
60	GAZGOA01(1)	Val-Ser	L	-20.83	-178.58	2.59	3.36	105.22	113.72

61	GAZGOA01(2)	Val-Ser	L	-20.90	-178.48	2.63	3.36	106.37	111.98
62	CAZGOA(2)	Val-Ser	L	-21.50	-178.23	2.64	3.36	106.17	112.27
63	MOBYEH(5)	Val-Phe	L	-21.63	-177.87	2.67	3.34	106.81	110.99
64	GAZGOA01(3)	Val-Ser	L	-22.23	-178.01	2.63	3.35	105.87	111.91
65	CAZGOA(3)	Val-Ser	L	-22.73	-177.57	2.64	3.35	105.85	111.96
66	AQASIU	Val-Val	L	-26.13	-179.89	2.59	3.44	112.09	109.52
67	MOBYAD	Val-Phe	L	-31.15	-177.50	2.70	3.27	106.75	112.35
68	NAYZET(3)	Val-Ala	L	-35.79	-178.33	2.71	3.25	106.60	112.26
69	MOBYEH(6)	Val-Phe	L	-37.29	-178.08	2.70	3.21	106.37	112.70
7ß	TIPTOB	Val-Gln	L	-40.11	-178.33	2.74	3.15	106.90	110.95
71	MOBYEH(7)	Val-Phe	L	-42.14	-181.45	2.70	3.13	105.25	111.39
72	FOBLUE	Val-Ser	L	-49.09	-176.76	2.84	3.08	108.37	110.10
73	COCGIK(1)	Val-Phe	L	-50.41	-177.21	2.83	3.05	107.45	110.33
74	COCGIK(2)	Val-Phe	L	-50.74	-178.32	2.84	3.05	107.58	110.33
75	CIJGUX	Val-Glu	L	-54.77	-180.70	2.86	3.05	107.66	111.04
76	MOBYEH(8)	Val-Phe	L	-55.34	-178.74	2.93	3.08	109.31	111.55
77	COCGIK(3)	Val-Phe	L	-60.53	-177.15	2.91	3.00	107.72	111.41
78	COCGIK(4)	Val-Phe	L	-61.36	-176.71	2.92	3.00	107.72	111.50
	Average			-32.57	-179.08	2.73	3.24	109.31	111.31

[a]Parenthesis () indicate independent molecules in the unit cell. [b]Compound excluded for average calculation. [c]*Syn*-conformation, rotation angle ψ: O_{trans}-C'-C_α-N, pyramidalization angle θ: O_{trasn}-C'-C_α-N.

Author Contributions

H.B. planned and guided the research project. H.B. and T.T. carried out the experimental work, analyzed the results participated in writing the manuscript.