Supporting Information

Control of Helix Formation by (E)- and (Z)-Double Bonds in Vinylogous γ-Peptides – A Way to Ion Channels and Monomolecular Nanotubes

*Carsten Baldauf, Robert Günther and Hans-Jörg Hofmann**

Institute of Biochemistry, Faculty of Biosciences, Pharmacy and Psychology, University of Leipzig,

Brüderstraße 34, D-04103 Leipzig, Germany

e-mail: hofmann@uni-leipzig.de

Contents

Coordinate files in the ‘pdb’-format are given for all hexamer structures and the undecamers H_{22}^{I} and H_{27}^{I}.

Table S1. DFT/B3LYP/6-31G* Backbone Torsion Angles[a] for the Unsubstituted (U) and γ-Methyl-Substituted (G) Blocked Conformers of **1** (n=1)

Conf.	φ	θ	ζ	ψ	Conf.	φ	θ	ζ	ψ
U1	-126.3	-126.4	-179.4	-177.6	G3a	-129.0	11.4	179.6	-176.3
					G3b	-134.9	9.7	177.2	27.3
U2a	-84.7	104.4	-178.4	178.2					
U2b	-87.9	123.3	176.1	33.6	G4a	64.7	122.2	179.5	-178.4
U2c	-95.5	111.9	-176.9	-28.8	G4b	59.9	118.5	176.5	23.1
					G4b'		→ G1c[b]		
U3a	-121.6	11.7	179.6	176.4	G4c	61.2	122.7	-178.3	-24.6
U3b	-121.3	9.7	177.0	26.7	G4c'		→ G1b[b]		
U3c	-113.5	6.5	-176.6	-31.2					
					G5a		→ G2a[b]		
U4a	-115.5	-121.9	177.1	29.2	G5b	-160.1	114.7	-178.1	-31.6
U4b	-114.8	-121.2	-176.5	-25.7					
					G6a	-165.2	-25.1	-177.9	178.2
G1a	-139.7	-128.6	179.9	178.1	G6b	-163.5	-23.5	178.1	29.3
G1b	-129.0	-124.8	176.5	30.2					
G1c	-124.6	-123.6	-177.2	-26.2	G7a	75.2	-6.7	-180.0	175.0
					G7b	71.3	9.4	175.7	33.8
G2a	-84.5	102.9	-178.3	177.8	G7b'	-122.0	5.9	-176.2	-31.3
G2a'	66.1	-127.6	-179.2	-175.1	G7c	75.0	5.5	-178.9	-23.3
G2b	-88.0	119.5	176.0	33.7					
G2b'	47.3	-148.2	179.7	-36.0					
G2c	-96.2	109.5	-176.7	-29.5					
G2c'	61.2	-150.5	-179.1	23.7					

[a] Torsion angles in degrees. [b] Optimization leads to the conformer after the arrow.

Table S2. PCM/HF/6-31G* Backbone Torsion Angles[a] for the Unsubstituted (U) and γ-Methyl- Substituted (G) Blocked Conformers of **1** (n=1)

Conf.	φ	θ	ζ	ψ	Conf.	φ	θ	ζ	ψ
U1	-113.2	-125.1	-179.1	-179.7	G3a	-95.1	-3.7	-179.4	179.2
					G3b	-131.6	8.8	176.6	30.5
U2a	-87.7	130.3	178.3	-180.0					
U2b	-87.1	130.2	175.6	30.0	G4a	63.8	122.3	178.8	-179.8
U2c	-86.0	131.2	-178.7	-28.6	G4b	64.1	122.0	175.7	28.8
					G4b'		→G1c[b]		
U3a	-93.4	-0.4	-179.8	179.7	G4c	63.5	121.4	-178.3	-27.7
U3b	-95.5	0.9	177.1	29.2	G4c'		→G1b[b]		
U3c	-93.4	-1.8	-176.8	-30.5					
					G5a	-130.2	125.9	178.9	179.9
U4a	-89.5	-123.7	177.6	29.0	G5b		→G2c[b]		
U4b	-87.4	-125.7	-176.2	-28.6					
					G6a		→G3a[b]		
G1a	-135.9	-128.4	-179.2	179.5	G6b	-102.3	-0.9	177.8	28.8
G1b	-132.0	-125.4	177.5	31.4					
G1c	-135.2	-128.0	-176.4	-31.2	G7a	72.6	7.6	178.1	-179.5
					G7b	72.3	8.9	174.9	30.7
G2a	-92.9	125.4	178.9	-179.2	G7b'	-92.0	-6.4	-176.2	-31.3
G2a'	60.6	-145.8	-177.2	-177.6	G7c	73.3	4.9	-178.8	-26.8
G2b	-91.6	124.5	176.0	29.4					
G2b'	63.2	-144.7	-173.7	-27.1					
G2c	-91.7	121.8	-177.6	-29.5					
G2c'	62.4	-144.7	-179.7	28.7					

[a] Torsion angles in degrees. [b] Optimization leads to the conformer after the arrow.

Table S3. DFT/B3LYP/6-31G* Backbone Torsion Angles[a] of all Periodic Hexamer Structures **1** (n=6) Derived from the Monomer Conformers U in Table 1

Conf.	φ	θ	ζ	ψ	Conf.[b]	φ	θ	ζ	ψ
$(U1)_6$	-122.7	-126.3	-179.5	177.0	$(U3b)_6$	-121.0	9.1	177.2	26.3
	-124.2	-126.2	-179.5	177.0		-114.2	10.2	177.2	26.8
	-126.3	-126.5	-179.6	177.4		-115.6	10.8	177.2	27.4
	-124.5	-125.7	-179.7	177.8		-111.6	10.5	177.2	27.0
	-121.8	-125.7	-179.8	177.7		-111.1	9.9	177.1	26.8
	-122.5	-125.7	-179.6	177.2		-114.0	9.2	177.2	25.1
$(U2a)_6$	-84.4	101.9	-178.4	177.5	$(U3c)_6$	-112.8	6.9	-177.1	-28.8
	-84.9	102.3	-178.1	176.8		-118.6	6.8	-177.1	-28.6
	-85.4	104.4	-178.8	177.1		-120.7	7.8	-177.0	-28.4
	-86.4	105.9	-178.8	177.7		-117.5	6.6	-176.9	-28.8
	-85.8	104.9	-178.8	177.3		-120.6	6.8	-176.9	-29.1
	-85.9	104.6	-178.5	177.7		-125.2	7.9	-176.5	-29.8
$(U2b)_6$	-80.0	124.1	177.4	32.1	$(U4a)_6$	-113.3	-122.1	177.4	26.3
	-77.8	117.3	178.4	31.5		-82.1	-122.2	177.9	24.1
	-79.5	115.6	178.4	30.5		-83.7	-121.7	177.6	24.5
	-80.7	117.3	178.1	30.8		-82.8	-122.9	178.0	23.3
	-80.1	118.4	177.9	32.7		-90.4	-122.1	177.5	24.2
	-81.9	120.4	176.7	33.1		-88.3	-121.9	177.3	27.6
$(U2c)_6(H_{27}^{II})$	-94.5	120.2	-177.8	-22.8	$(U4b)_6$	-87.0	-123.6	178.2	23.1
	-111.8	125.8	-177.4	-24.7		-78.8	-122.1	-176.6	-26.0
	-81.9	136.0	176.2	37.6		-116.0	-122.9	-176.6	-25.4
	127.8	125.1	-176.2	-25.9		-117.7	-124.0	-176.0	-26.2
	-80.8	97.1	-172.9	-38.1		-115.3	-123.8	-175.9	-27.2
	-87.4	106.6	-175.8	-34.3		-124.8	-122.7	-176.3	-26.7
$(U3a)_6$	-113.5	10.7	178.7	-175.2					
	-103.5	9.9	178.5	-175.4					
	-105.3	9.7	178.9	-176.3					
	-107.1	10.2	178.9	-176.4					
	-108.6	10.0	178.9	-176.3					
	-113.9	11.4	179.6	-176.8					

[a] Angles in degrees.

Table S4. DFT/B3LYP/6-31G* Backbone Torsion Angles[a] for the Hydrogen-Bonded Helical Structures of the Hexamer **1** (n=6) Found in the Oligomer Approach

Conf.[b]	φ	θ	ζ	ψ	Conf.[b]	φ	θ	ζ	ψ
H_{14}	67.8	18.6	-164.3	165.7	H_{22}^{II}	114.6	-125.5	176.8	28.4
	65.0	12.9	-163.0	166.0		103.1	-117.3	173.1	33.7
	65.6	15.5	-162.7	161.8		99.4	-108.3	172.7	34.3
	65.5	16.4	-163.6	162.2		91.2	-104.6	172.6	35.1
	68.6	12.3	-163.1	155.3		85.0	-101.9	170.4	38.9
	84.1	-7.1	-179.2	178.8		88.0	-101.5	173.3	38.1
H_{17}	-152.6	-131.1	175.9	14.0	H_{24}	75.9	-118.9	175.4	32.1
	81.7	-100.8	163.7	35.8		73.8	-127.7	171.4	38.2
	95.0	-99.3	166.3	37.6		82.7	-118.3	177.5	-35.6
	83.2	-97.6	163.8	46.3		104.3	-116.1	171.6	29.6
	85.8	-96.9	162.7	42.4		95.3	-116.6	-177.5	-20.9
	82.5	-91.6	169.5	44.1		104.3	-129.5	-174.1	-19.6
H_{19}	78.1	7.8	171.6	-175.6	H_{27}^{I}	117.7	111.2	179.9	167.4
	69.3	31.1	-171.7	174.4		74.0	113.3	177.5	166.8
	84.4	12.7	-171.4	-173.3		73.1	108.1	179.0	161.6
	88.7	10.9	-169.9	179.0		68.1	108.5	179.0	163.7
	92.2	12.3	-174.1	-177.3		70.8	117.2	177.9	171.1
	117.7	-3.9	-179.1	-176.9		78.4	127.2	177.4	177.1
H_{22}^{I}	122.1	115.8	-178.4	167.6	H_{27}^{II}	-94.5	120.2	-177.8	-22.8
	75.8	104.2	-175.9	159.5		-111.8	125.8	-177.4	-24.7
	64.8	106.0	-174.2	159.5		-81.9	136.0	176.2	37.6
	72.3	106.2	-172.8	160.6		127.8	125.1	-176.2	-25.9
	70.8	105.0	-176.0	160.4		-80.8	97.1	-172.9	-38.1
	72.2	131.2	178.0	-175.6		-87.4	106.6	-175.8	-34.3

[a] Angles in degrees. [b] H_x denotes a helix with x-membered hydrogen-bonded pseudocycles.

Table S5. Relative Enthalpies, Free Enthalpies, Entropies, and Total Energies[a] at the HF/6-31G* level of ab initio MO theory of the Conformers of **1** (n=6)

Conf.[b]	ΔH	ΔG	ΔS	E_T
$(U1)_6$	32.8	**0.0**	**0.0**	-1949.197490
$(U2a)_6$	42.2	19.1	-32.4	-1949.193825
$(U2b)_6$	102.5	82.3	-42.3	-1949.170561
$(U3a)_6$	28.3	13.0	-58.7	-1949.198833
$(U3b)_6$	105.5	88.6	-53.2	-1949.169537
$(U3c)_6$	90.8	70.6	-42.2	-1949.175084
$(U4a)_6$	66.2	54.1	-69.6	-1949.185375
$(U4b)_6$	79.9	56.3	-30.6	-1949.179535
H_{14}	41.8	72.8	-213.7	-1949.196331
H_{17}	68.3	95.8	-202.1	-1949.185944
H_{19}	4.2	30.6	-198.5	-1949.209514
H_{22}^{I}	**0.0**	21.4	-181.7	-1949.211533
H_{22}^{II}	65.3	78.1	-152.8	-1949.186045
H_{24}	73.1	89.4	-164.9	-1949.183072
H_{27}^{I}	14.9	26.5	-148.9	-1949.204979
$H_{27}^{II}/(U2c)_6$	61.5	69.7	-137.5	-1949.187053

[a] Relative enthalpies and relative free enthalpies in kJ/mol; relative entropies in J/mol·K; total energies in a.u. [b] H_x denotes a helix with x-membered hydrogen-bonded pseudocycles.

Table S6. DFT/B3LYP/6-31G* Backbone Torsion Angles[a] for the Unsubstituted and γ-Methyl-Substituted (G) Blocked Conformers of **2** (n=1)

Conf.	φ	θ	ζ	ψ	Type[b]	Conf.	φ	θ	ζ	ψ	Type[b]
U1	91.1	69.2	-0.5	168.1	C_7	G4	-69.5	154.3	-1.4	-166.9	
U2	81.3	-119.7	-2.0	42.5	C_9	G5	62.3	138.9	-0.7	-175.0	
U3	117.9	128.5	-0.8	44.5		G6		→ G2[c]			
U4	177.8	-82.0	-2.7	29.7	C_7*	G7	-159.0	122.9	-3.5	46.2	
U5	-123.6	-127.2	-1.4	48.1		G8	63.2	123.7	-0.7	43.7	
U6	107.5	44.1	-0.2	35.0		G9	66.5	-117.3	2.4	63.1	C_9^{ax}
U7	127.5	-135.3	2.9	-38.2		G10	57.5	86.8	-2.2	-33.7	C_7*
						G11	-95.2	-18.2	-1.3	-65.3	
G1	-81.2	118.9	1.7	-43.2	C_9^{eq}	G12	-70.7	-65.1	1.5	29.5	C_7*
G2	-113.6	-47.7	0.0	-177.8	C_7^{ax}	G13	-160.8	-56.7	-2.5	13.8	C_7*
G3	61.9	73.1	-1.0	170.4	C_7^{eq}						

[a] Torsion angles in degrees. [b] C_x denotes a hydrogen-bonded pseudocycle with *x* atoms, *eq, ax*: pseudoequatorial or pseudoaxial orientation of the C(*γ*) substituents. An asterisk denotes NH···N hydrogen bonding. [c] Optimization leads to the conformer after the arrow.

Table S7. PCM/HF/6-31G* Backbone Torsion Angles[a] for the Unsubstituted and γ-Methyl-Substituted (G) Blocked Conformers of **2** (n=1)

Conf.	φ	θ	ζ	ψ	Type[b]	Conf.	φ	θ	ζ	ψ	Type[b]
U1	88.5	119.8	0.0	168.5	C_7	G4	-93.2	144.3	0.0	-167.3	
U2	80.4	-123.2	0.6	45.2	C_9	G5	65.5	141.1	-0.1	-171.4	
U3	89.1	128.6	-0.6	54.1		G6		→ G4[c]			
U4	-131.0	-125.0	0.3	59.8	C_7*	G7	-141.0	120.1	-1.4	66.9	
U5	-91.6	-125.0	0.1	59.1		G8	64.3	118.1	-1.2	69.0	
U6	82.4	15.3	0.3	77.8		G9	66.0	-120.0	4.5	63.0	C_9^{ax}
U7	88.1	-139.0	1.8	-52.1		G10	62.7	119.3	-1.0	-60.7	C_7*
						G11	-83.4	-16.4	1.0	-83.2	
G1	-81.6	122.3	0.0	-46.3	C_9^{eq}	G12	-72.9	-74.8	0.8	52.7	C_7*
G2	-108.7	-46.0	-0.8	175.8	C_7^{ax}	G13	-160.1	-70.9	-2.1	35.5	C_7*
G3	58.6	93.5	-2.1	168.6	C_7^{eq}						

[a] Torsion angles in degrees. [b] C_x denotes a hydrogen-bonded pseudocycle with *x* atoms, *eq, ax*: pseudoequatorial or pseudoaxial orientation of the C(*γ*) substituents. An asterisk denotes NH···N hydrogen bonding. [c] Optimization leads to the conformer after the arrow.

Table S8. DFT/B3LYP/6-31G* Backbone Torsion Angles[a] of all Periodic Hexamer Structures either Derived from the Monomers U in Table 6 or Obtained in the Oligomer Approach on Hexamers of **2** (n=6)

Conf.[b]	φ	θ	ζ	ψ	Conf.[b]	φ	θ	ζ	ψ
$H_7(U1)_6$	96.8	66.5	-0.4	169.4	H_{14}	110.2	-126.6	2.1	150.7
	99.7	65.1	-0.5	168.8		77.3	-102.0	-8.2	136.1
	97.9	64.9	-0.4	168.9		125.1	-114.7	0.3	62.0
	97.7	64.4	-0.4	169.4		176.9	-114.7	1.7	67.2
	99.2	63.8	-0.3	170.0		132.8	-95.2	-4.6	140.4
	97.2	67.0	-0.6	167.4		82.4	-105.0	-6.3	133.1
$H_9(U2)_6$	81.2	-119.3	-0.9	45.0	H_{17}	-115.6	-110.7	-3.2	137.7
	83.8	-119.2	-0.6	43.6		169.0	-97.9	-3.9	136.0
	83.0	-119.3	-0.6	44.0		164.6	-81.7	0.2	151.4
	83.7	-118.7	-0.6	42.0		143.7	-83.2	-1.0	165.9
	82.6	-120.0	-0.5	44.7		134.9	-58.9	-4.2	129.1
	83.4	-119.4	-1.4	40.8		-149.6	-151.3	0.5	172.1
H_{12}	74.9	80.3	-5.8	39.3	$(U3)_6$	116.7	129.3	-0.7	44.8
	66.6	70.8	-2.0	62.1		128.6	130.9	-1.2	44.1
	63.8	64.6	-3.5	64.8		129.1	129.1	-1.2	45.8
	66.9	64.4	-3.3	66.8		132.3	131.0	-1.2	44.6
	66.6	61.4	-1.6	62.7		128.5	129.8	-1.2	45.1
	62.4	70.5	-2.4	74.2		132.5	129.5	-1.3	43.9

[a] Angles in degrees. [b] H_x denotes a helix with hydrogen-bonded pseudocycles with *x* members.

Table S9. Relative Enthalpies, Free Enthalpies, Entropies, and Total Energies[a] at the HF/6-31G* level of ab initio MO theory of the Conformers of **2** (n=6)

Conf.[b]	ΔH	ΔG	ΔS	E_T
$H_7(U1)_6$	**0.0**	**0.0**	-62.1	-1949.204844
$H_9(U2)_6$	1.2	24.2	-139.3	-1949.205023
H_{12}	91.7	118.2	-151.0	-1949.168785
H_{14}	57.6	86.0	-157.4	-1949.181578
H_{17}	75.0	93.1	-122.6	-1949.174645
$(U3)_6$	135.7	117.2	**0.0**	-1949.150232

[a] Relative enthalpies and relative free enthalpies in kJ/mol; relative entropies in J/mol·K; total energies in a.u. [b] H_x denotes a helix with x-membered hydrogen-bonded pseudocycles.

Table S10. HF/6-31G* Backbone Torsion Angles[a] of Selected Undecamer Structures

1 (n=11)

Conf.[b]	φ	θ	ζ	ψ
H_{19}	77.8	14.6	-173.5	-174.9
	71.7	29.7	-172.5	-172.4
	76.8	21.6	-172.4	-173.3
	74.7	23.7	-172.6	-171.9
	76.0	27.3	-172.8	-174.9
	74.2	26.0	-172.6	-173.8
	73.3	29.6	-173.1	-176.0
	76.0	22.2	-173.2	-172.9
	83.0	21.6	-172.7	177.2
	84.5	15.2	-175.5	-176.4
	115.7	-1.4	179.5	-175.5
H_{22}^{I}	115.1	116.5	-177.9	164.2
	73.9	107.0	-175.3	156.6
	68.8	108.9	-173.2	158.1
	70.5	108.5	-172.8	159.0
	71.5	111.0	-173.7	156.5
	69.0	110.5	-173.0	158.7
	70.8	109.6	-172.6	158.1
	67.9	113.3	-173.9	158.4
	69.8	109.3	-173.1	156.2
	68.7	111.0	-175.6	161.5
	74.1	130.0	178.9	-177.0
H_{27}^{I}	101.0	114.3	-179.9	166.3
	78.9	108.7	179.2	161.9
	73.2	112.0	179.4	161.2
	72.0	110.0	-179.3	161.0
	71.7	112.4	-179.3	163.0
	74.7	111.6	-179.2	158.6
	69.8	116.5	-179.8	161.5
	73.0	112.2	-179.4	159.9
	71.3	112.9	179.5	160.2
	71.5	118.1	177.8	165.9
	75.8	131.9	176.8	-179.9

[a] Angles in degrees. [b] H_x denotes a helix with x-membered hydrogen-bonded pseudocycles;

total energies:

H_{19}: E_T=-3367.732121 a.u.
H_{22}^{I}: E_T=-3367.740976 a.u.
H_{27}^{I}: E_T=-3367.732464 a.u.