Randomization of Oligopeptide Conformations by Nearest Neighbor Interactions between Amino Acid Residues

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Supporting Information

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J-coupling constants [Hz]	GAFG	GA**F**G	G**F**AG	GF**A**G
$^{3}J(H^{N}H^{\alpha})$	Exp: 6.24 Gauss: 6.08	Exp: 7.67 Gauss: 7.78	Exp: 6.92 Gauss: 6.98	Exp: 7.02 theo: 6.81
$^{3}J(H^{N}C')$	Exp: 1.21 Gauss: 1.04	Exp: 0.33 Gauss: 0.76	Exp: 1.01 Gauss: 0.97	Exp: 1.14 Gauss: 1.03
$^{3}J(H^{\alpha}C')$	Exp: 2.2 Gauss:2.4 2	Exp: 2.48 Gauss: 2.43	Exp: 2.22 Gauss: 2.24	Exp: 2.08 Gauss: 2.24
$^{3}J(H^{N}H^{\beta})$	Exp: 1.94 Gauss: 1.96	Exp: 1.26 Gauss: 1.38	Exp: 1.81 Gauss: 1.65	Exp: 2.06 Gauss:1.63
$^{1}J(H^{N}H^{\alpha})$	-		Exp: 11.7 Gauss: 11.63	Exp: 11.3 Gauss: 11.4
χ_r^2	5.49	8.17	0.2	1.67

Table S1: Experimental and calculated (Gauss) J-coupling constants of the indicated residues of the cationic tetrapeptides GAFG and GFAG. The respective residues are typed in bold in the header. The reduced chi-square value of the fits are listed at the bottom of the table.

Basins	GAG	G**A**FG	GF**AG**	GFG	G**F**AG	GA**F**G
pPII	−72°,150°	−73°,150°	−73°,150°	−77°,155°	−72°,152°	−74°,152°
β-strand	−115°,150°	−120°,150°	−115°,150°	−115°,155°	−120°,150°	−115°,150°
iγ	−60°,60°	−60°,60°	−60°,60°	−80°,60°	−80°,60°	−80°,60°
rh	−60°,−30°	−60°,−30°	−60°,−30°	−65°,−20°	−65°,−30°	−65°,−30°
lh/γ	60°,−60°	70°,50°	70°,50°	80°,20°	75°, 60°	80°,60°

Table S2: Positions of Gaussian sub-distributions representing basins in the Ramachandran plot of the indicated peptides

J-coupling constants [Hz]	G**K**KG	GK**K**G
$^{3}J(H^{N}H^{\alpha})$	Exp: 6.42 Gauss: 6.47	Exp: 7.05 Gauss: 6.93
$^{3}J(H^{N}C')$	Exp: 0.91 Gauss: 0.96	Exp: 1.11 Gauss: 1.96
$^{3}J(H^{\alpha}C')$	Exp: 1.95 Gauss:2.0	Exp: 1.75 Gauss: 1.97
$^{3}J(H^{N}H^{\beta})$	Exp: 1.83 Gauss: 1.96	Exp: 1.54 Gauss: 1.38
$^{1}J(H^{N}H^{\alpha})$	Exp: 11.79 Gauss: 11.72	Exp:11.60 Gauss: 11.60
χ_r^2	0.25	0.72

Table S3: Experimental and calculated (Gauss) J-coupling constants of the indicated residues of the cationic tetrapeptide GKKG. The respective residues are typed in bold in the header. The reduced chi-square value of the fits are listed at the bottom of the table.

Conformation	GK G	G**K**K G	GK**K** G
pPII	0.5	0.81	0.54
β-strand	0.41	0.156	0.46
iγ/type II β	0.0	0.04	0
rh	0.09	0	0
lh/γ	0.0	0.14	0

Table S4: List of statistical weights of conformations constituting the Ramachandran plots of the indicated peptides.

Basins	GK G	G**K**K G	GK**K** **G**
pPII	−66°,150°	−74°,155°	−66°,150°
β-strand	−115°,145°	−115°,155°	−115°,150°
iγ		−60°,30°	−20°,20°
rh	−65°,−30°	−65°,−30°	−65°,−30°
lh/γ		60°,30°	20°,−50°

Table S5: Positions of Gaussian sub-distributions representing basins in the Ramachandranplot of the indicated peptides.

	pPII	ß-strand	rh+iγ+type I' ß	lh+γ
GA*G	0.80	0.10	0.06	0.04
GA*AG	0.76	0.14	0.10	0.00
GAA*G	0.78	0.13	0.09	0.00
AA*AA	0.90	0.00	0.00	0.10
AAA*A	0.88	0.00	0.00	0.12

	pPII	ß-strand	rh+iγ+type I' ß	asx-turn
GD*G	0.30	0.39	0.09	0.23
GD*DG	0.28	0.28	0.21	0.23
GDD*G	0.12	0.61	0.20	0.06
GD*DDG	0.27	0.38	0.13	0.22
GDD*DG	0.33	0.30	0.37	0.00
GDDD*G	0.31	0.34	0.21	0.15

	pPII	ß-strand	rh+iγ+type I' ß	asx-turn
GR*G	0.58	0.20	0.14	0.08
GR*RG	0.69	0.16	0.15	0.01
GRR*G	0.45	0.33	0.22	0.00
GR*RRG	0.69	0.29	0.02	0.00
GRR*RG	0.39	0.44	0.16	0.00
GRRR*G	0.53	0.38	0.09	0.00

Table S6: Statistical weight of the indicated conformations in the Ramachandran plots of alanine, aspartic acid and arginine based homopeptide sequences. Values were taken from ref. [43–45,51]

	$\delta G_{pPII\beta,12}$	$\delta G_{\beta pPII,12}$	$\delta G_{pPII\beta,21}$	$\delta G_{\beta pPII,21}$
GRRG	2.2±0.5	1.0±0.3	−0.1±0.3	2.0±0.3

	$\delta G_{tlpPII,12}$	$\delta G_{tlpPII,21}$
GRRG	2.7±1.0	1.7±0.8

	$\delta G_{pPII\beta,12}$	$\delta G_{\beta pPII,12}$	$\delta G_{pPII\beta,23}$	$\delta G_{\beta pPII,23}$	$\delta G_{pPII\beta,32}$	$\delta G_{\beta pPII,32}$
GRRRG	0.8±0.7	1.6±0.6	0.1±0.6	0.7±0.6	−1.1±0.7	1.4±0.6

	$\delta G_{pPII\beta,12}$	$\delta G_{\beta pPII,12}$	$\delta G_{pPII\beta,21}$	$\delta G_{\beta pPII,21}$
GDDG	0.2±0.5	−0.5±0.5	−2.7±0.6	1±0.6

	$\delta G_{tlpPII,12}$	$\delta G_{tlpPII,21}$
GDDG	1.8±1.0	2.0±0.8

	$\delta G_{pPII\beta,12}$	$\delta G_{\beta pPII,12}$	$\delta G_{pPII\beta,23}$	$\delta G_{\beta pPII,23}$	$\delta G_{pPII\beta,32}$	$\delta G_{\beta pPII,32}$
GDDDG	0.2±0.5	0.2±0.5	3.8±0.5	0.7±0.4	−0.6±0.5	−0.7±0.4

	$\delta G_{tlpPII,12}$	$\delta G_{tlpPII,21}$
GDDDG	1.1±1.0	2.0±0.8

Table S7: Parameters reflecting nearest neighbor interactions in the indicated peptides. In addition to pPII-β NNIs we list some interaction parameters involving right-handed helical and turn conformations for which the statistical error is not larger than the value itself.

x,y	$\delta G_{pPII\beta,12}$	$\delta G_{\beta pPII,12}$	$\delta G_{pPII\beta,21}$	$\delta G_{\beta pPII,21}$	$\delta G_{pPIItl,12}$	$\delta G_{tlpPII,12}$	$\delta G_{pPIItl,21}$	$\delta G_{tlpPII,21}$
AV	−2.9±0.5	3.2±0.5	0.7±0.3	0.3±0.5	1.3±0.6	1.7±1.0	-	-
DA	−0.1±0.4	1.1±0.3	−2.6±0.4	0.3±0.5	-	-	−2.0±1.0	-
AL	−0.3±0.5	3±0.5	0.1±0.5	0.2±0.4	-	-	-	-
AF	2±0.5	0.2±0.3	−0.9±0.4	0.2±0.5	4.0±1.0	-	−1.4±1.0	-
FA	1.7±0.5	0.2±0.4	−3±0.7	0.5±0.5	-	−2.0±1.0	-	-

x,y	$\delta G_{pPII\beta,12}$	$\delta G_{\beta pPII,12}$	$\delta G_{(pPII\beta,21)}$	$\delta G_{\beta pPII,21}$	$\delta G_{pPIItl,12}$	$\delta G_{tlpPII,12}$	$\delta G_{pPIItl,21}$	$\delta G_{tlpPII,21}$
DA	−0.1±0.4	1.1±0.3	−2.6±0.4	0.3±0.5	-	-	−2.0±1.0	-
DV	3.1±0.3	2.2±0.3	0.1±0.5	0.4±0.3	-	-	-	-
DD	−0.2±0.5	−0.5±0.5	−2.7±0.6	1.0±0.7	-	1.8±1.0	-	2.0±1.0
DL	2.7±0.3	−2.3±0.3	0.6±0.5	0.4±0.5	-	-	-	-
FD	6.0±0.4	0.7±0.4	−0.6±0.5	−0.3±0.6	-	1.5±1.0	-	1.7±1.0
DF	1.6±0.3	1.5±0.3	−1±0.4	0.1±0.5	-	-	-	-

x,y	$\delta G_{pPII\beta,12}$	$\delta G_{\beta pPII,12}$	$\delta G_{pPII\beta,21}$	$\delta G_{\beta pPII,21}$	$\delta G_{pPIItl,12}$	$\delta G_{tlpPII,12}$	$\delta G_{pPIItl,21}$	$\delta G_{tlpPII,21}$
AV	−2.9±0.5	3.2±0.5	0.7±0.3	0.3±0.5	1.3±0.6	1.7±1.0	-	-
SV	1.5±0.4	2.1±0.4	−0.5±0.4	0.1±0.5	-	-	-	-
DV	3.1±0.3	2.2±0.3	0.1±0.5	0.4±0.3	-	-	-	-

Table S8: Parameters reflecting nearest neighbor interactions in the indicated peptides. In addition to pPII-β NNIs we list some interaction parameters involving right-handed helical and turn conformations for which the statistical error is not larger than the value itself.

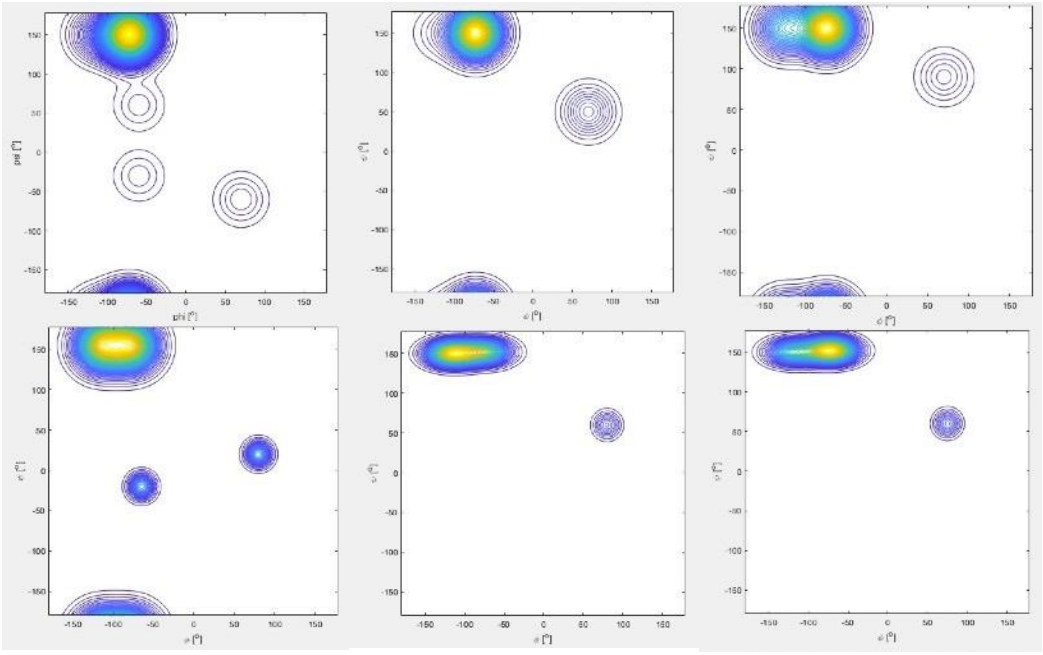

Figure S1: Upper panel: Ramachandran plots of GAG (left), G**A**FG (middle) and GF**A**G (right); Lower panel: Ramachandran plots of GFG (left), GA**F**G(middle) and G**F**AG (left).

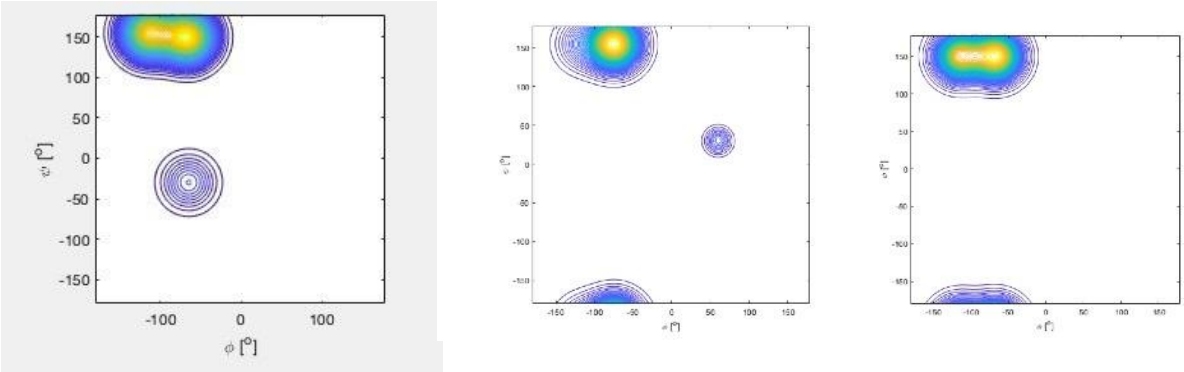

Figure S2: Ramachandran plot of GKG (left), G**K**KG (middle) and GK**K**G (right).