SUPPORTING INFORMATION

Temperature Dependence of Looping Rates in a Short Peptide

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Table S-1: Relative conformational energy of the Dbo fragment used for the parameterization. *t* and *c* indicate a *trans* and *cis* amide bond conformation (angle χ^3 in Scheme 2).

conformer	χ_1	χ_2	ΔE/(kJ/mol)
I_t	56.0	114.0	0
II_t	–55.5	117.3	19.8
III_t	–176.4	–102.4	11.2
I_c	66.0	100.0	21.7
II_c	–56.5	143.4	18.8
III_c	–178.7	–122.3	23.3

Table S-2: Symmetry-averaged CHELPG partial charges of the lowest energy conformer of Dbo in its electronic ground state.[a]

atom number	atom name	S_0	atom number	atom name	S_0
1	C	–0.249	15	H	0.014
2	C	0.690	16	H	0.070
3	N	–0.466	17	H	–0.070
4	N	–0.268	18	H	–0.047
5	C	0.609	19	H	0.144
6	C	0.197	20	H	0.144
7	C	0.197	21	H	0.206
8	C	–0.249	22	H	–0.070
9	C	–0.453	23	H	–0.047
10	N	–0.367	24	H	0.070
11	C	0.855	25	H	0.014
12	O	–0.689	26	H	0.147
13	C	–0.532	27	H	0.128
14	H	–0.126	28	H	0.147

[a] Calculated dipole moment was 2.1 Debye.

Table S-3: GROMOS96 force field parameters for the synthetic amino acid Dbo. Only the parameters different/modified from the natural amino acid asparagine are reported. Charges are in electrostatic units.

atom number	atom type	*q*/e
CH_2	CH2	–0.20
C1	C	0.50
N1	NR	–0.30
C2	CH2	0.15
C3	CH2	–0.15
C5	CH2	–0.15
C6	CH2	0.15
C4	CH1	0.47
N2	NR	–0.47

bond	length/nm
CH_2-C1	0.152
C1-C2	0.154
C1-N1	0.147
C1-C6	0.154
C2-C3	0.154
C3-C4	0.154
C4-C5	0.154
C4-N2	0.147
C5-C6	0.154
N1-N2	0.122

Table S-3 (continued): GROMOS96 force field parameters for the synthetic amino acid Dbo. Only the parameters different/modified from the natural amino acid asparagine are reported. Charges are in electrostatic units.

bond angle	θ_0/degrees	K_θ/(kJmol^{-1}rad^{-2})
Nδ - CH_2 - C1	112	520
CZ - C1 - C2	113	520
CZ - C1 - N1	108	520
CZ - C1 - C6	112	520
C1 - C2 - C3	108	520
C1 - N1 - N2	116	520
C1 - C6 - C5	108	520
C2 - C3 - C4	116	520
C2 - C1 - N1	108	520
C2 - C1 - C6	109	520
C3 - C4 - C5	110	520
C3 - C4 - N2	108	520
C4 - C5 - C6	108	520
C4 - N2 - N1	115	520
C5 - C6 - C1	108	520
C5 - C4 - N2	108	520
C6 - C1 - N1	107	520

dihedral bond angle	ϕ_0/degrees	K_ϕ/(kJmol^{-1}rad^{-2})	multiplicity
Nδ - CH_2 - C1 - N1	0.0	3.5	3
Nδ - CH_2 - C1 - N1	0.0	0.4	2
Nδ - CH_2 - C1 - N1	0.0	0.3	1

Table S-4: Fluorescence lifetimes (τ) of the Dbo-AlaGlyGln-Trp-NH_2 peptide, fluorescence lifetimes of the quencher-unlabeled reference peptide[a] (τ_0), and calculated looping rates[b] (k_{loop}) in D_2O.

T/K	τ/ns [c]	τ_0/ns [a,d]	$k_{loop}/(10^7$ $sec^{-1})$[b,e]
283	23.5	613	4.1
288	20.4	569	4.7
293	17.0	530	5.7
298	14.3	496	6.8
303	12.2	468	8.0
308	10.6	442	9.2
313	9.3	421	10.5
318	8.2	402	11.9
323	7.1	386	13.7
328	6.3	372	15.6
333	5.6	360	17.5
338	4.9	350	19.9

[a] $(Gly)_6$-Dbo was used as reference peptide (without quencher). [b] Calculated as $k_{loop} = 1/\tau - 1/\tau_0$. [c] Error ± 3%. [d] Error ± 5 ns. [e] Error ± 10%.