Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Supplementary Information

for

Trp-Trp pairs as β-hairpin stabilisers: Hydrogen-bonded *versus* non-hydrogen-bonded sites

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Table S1. ^{1}H, ^{13}C and ^{15}N chemical shifts (ppm, from DSS) for peptide **W2W11** in D_2O at pH 5.5 and 5ºC, except for those of HN amide that were measured in H_2O/D_2O 9:1 v/v. Values for the Pro residue in the minor *cis* species are in italics.

Residue	^{15}N	NH	$^{13}C_\alpha$	$C_\alpha H$	$^{13}C_\beta$	$C_\beta H$	Others
M1			54.9	4.12	32.8	2.15, 2.15	$^{13}C_\gamma$ 30.7; $C_\gamma H$ 2.56, 2.56; $^{13}C_\varepsilon$ 16.7; $C_\varepsilon H_3$ 2.08
W2	125.6	8.88	58.0	4.66	29.5	3.21, 3.21	$C_{\delta 1}H$ 7.25; $N_{\varepsilon 1}H$ 10.22; $C_{\varepsilon 3}H$ 7.57; $C_{\zeta 3}H$ 7.13; $C_{\eta 2}H$ 7.21; $C_{\zeta 2}H$ 7.49
V3	125.9	7.84	61.1	3.83	33.6	1.73	$^{13}C_\gamma$ 20.9; $C_\gamma H_3$ 0.71; $^{13}C_{\gamma'}$ 20.9; $C_{\gamma'}H_3$ 0.78
N4	124.8	8.29	50.9	4.27	38.6	2.52, 2.84	$^{15}N_\delta$ 113.6; $N_\delta H$ 7.18, 7.85
P5			63.6	4.33 *4.75*	32.2	1.96, 2.26 *2.11, 2.33*	$^{13}C_\gamma$ 27.2; $C_\gamma H$ 2.05, 2.05; *1.87, 1.93* $^{13}C_\delta$ 51.0; $C_\delta H$ 3.84, 3.84; *3.59, 3.49*
R6	119.4	8.29	56.5	4.28	30.4	1.75, 1.84	$^{13}C_\gamma$ 27.3; $C_\gamma H$ 1.55, 1.63; $^{13}C_\delta$ 43.2; $C_\delta H$ 3.15, 3.15; $^{15}N_\varepsilon$ 84.4; $N_\varepsilon H$ 7.22
T7	113.9	7.99	61.9	4.30	69.7	4.24	$^{13}C_\gamma$ 21.6; $C_\gamma H_3$ 1.17; $O_\gamma H$ 5.71
Q8	122.4	8.34	56.0	4.23	29.3	1.95, 2.05	$^{13}C_\gamma$ 33.7; $C_\gamma H$ 2.26, 2.26; $^{15}N_\varepsilon$ 113.0; $N_\varepsilon H$ 6.90, 7.55
S9	117.1	8.40	58.6	4.39	63.7	3.67, 3.74	$O_\gamma H$ 5.81
S10	117.5	8.30	58.6	4.41	63.7	3.79, 3.79	
W11	122.7	8.10	57.1	4.72	29.6	3.29, 3.29	$C_{\delta 1}H$ 7.22; $^{15}N_{\varepsilon 1}$ 129.6; $N_{\varepsilon 1}H$ 10.16; $C_{\varepsilon 3}H$ 7.60; $C_{\zeta 3}H$ 7.13; $C_{\eta 2}H$ 7.22; $C_{\zeta 2}H$ 7.47
M12	126.7	7.71	57.2	4.17	33.8	1.83, 1.99	$^{13}C_\gamma$ 32.1; $C_\gamma H$ 2.27, 2.27; $^{13}C_\varepsilon$ 16.8; $C_\varepsilon H_3$ 2.03

Table S2. List of upper limit distance restraints (Å) used for structure calculation of peptide **W2W11** (24 in total). The Q stands for pseudo atoms, virtual atoms used for structure calculation, which in the case of a methyl group is equidistant from the three protons, and in the case of methylene and amide groups equidistant from the two geminal protons.

2	TRP	HE1	4	ASN	HA	5.50
4	ASN	HN	8	GLN	HB2	3.80
4	ASN	HN	8	GLN	HB3	3.80
4	ASN	HN	8	GLN	QG	6.38
4	ASN	HD21	6	ARG	HB2	7.23
4	ASN	HD21	6	ARG	HB3	7.23
6	ARG	HN	8	GLN	HB2	3.80
6	ARG	HN	8	GLN	HB3	3.80
6	ARG	HN	8	GLN	QG	6.38
2	TRP	HZ3	4	ASN	HA	5.50
2	TRP	HZ2	4	ASN	HA	4.38
2	TRP	HZ2	5	PRO	QG	6.38
2	TRP	HZ2	5	PRO	QD	5.35
2	TRP	HH2	4	ASN	HA	4.76
4	ASN	HA	5	PRO	QD	3.71
2	TRP	HZ3	4	ASN	QB	5.85
2	TRP	HH2	4	ASN	QB	6.32
3	VAL	QQG	5	PRO	HA	8.09
3	VAL	QQG	5	PRO	QB	8.13
4	ASN	QB	7	THR	HN	5.14
4	ASN	QD2	6	ARG	QB	6.31
4	ASN	HD22	6	ARG	HB2	7.23
4	ASN	HD22	6	ARG	HB3	7.23
4	ASN	QD2	7	THR	QG2	7.40

Table S3. List of dihedral angle restraints (º) used for structure calculation of peptide **W2W11** (9 for φ angles and 5 ψ; 14 in total).

2	TRP	PHI	-163.0	-15.6
2	TRP	PSI	99.2	163.4
3	VAL	PHI	-168.9	-37.5
3	VAL	PSI	105.8	160.6
4	ASN	PHI	-156.8	-22.6
4	ASN	PSI	84.5	190.7
6	ARG	PHI	-103.2	-56.6
6	ARG	PSI	-56.0	-15.3
7	THR	PHI	-180.0	0.0
8	GLN	PHI	-117.5	-38.6
8	GLN	PSI	-60.1	6.6
9	SER	PHI	-180.0	0.0
10	SER	PHI	-180.0	0.0
11	TRP	PHI	-180.0	0.0