Table I

Chemical shift assignments for HP21at pH5.5, 12 ^{o}C.

Residue	NH	αCH	βCH	Others
L42	8.95	4.65	1.86, 1.72	δCH_3 0.98
S43	9.39	4.51	4.35, 4.10	
D44	9.05	4.46	2.73	
E45	8.77	4.13	2.35, 2.02	
D46	8.13	4.54	2.82, 2.71	
F47	8.91	4.13	3.34, 3.06	δ1CH, δ2CH7.30; ε1CH, ε2CH6.92; ςCH6.42
K48	8.00	4.29	1.91	γ$CH_2$1.42,1.34;δ$CH_2$1.67; ε$CH_2$3.01,2.90; NH7.14
A49	7.81	4.15	1.50	
V50	7.91	3.69	1.61	γCH_3 0.85,0.14
F51	8.48	4.40	2.95, 2.49	δ1CH, δ2CH6.61; ε1CH, ε2CH7.10; ςCH7.03
G52	8.18	4.10, 3.91		
M53	7.78	4.79	2.38, 2.13	γCH_2 2.79,2.49
T54	8.25	4.54	4.38	γCH_3 1.37
R55	8.70	4.61	1.48, 1.37	γ$CH_2$1.07,0.74;δ$CH_2$3.66;NH7.13
S56	8.39	4,21	3.86, 3.80	
A57	7.97	4.18	1.45	
F58	8.41	4.43	3.20, 3.12	δ1CH, δ2CH7.26
A59	8.08	4.16	1.45	
N60	7.84	4.65	2.90, 2.73	
L61	7.74	4.18	1.75, 1.67	γCH1.50;δ$CH_3$0.85

Table II

Deviation of $C_\alpha H$ chemical shifts from random coil values (Δ), the calculated ring current contributions to the native state $C_\alpha H$ chemical shifts and the measured $^3J_{NH,\alpha}$ coupling constants for HP21 and for the smaller peptide fragments. Ring current contributions were calculated using the method of Case, http://www.scripps.edu/mb/case/qshifts/qshifts.htm , inputting the structure of HP21 region of the intact helical subdomain.

Residue	Δ[(a)]	Ring current shift[(b)]	Ring current shift[(c)]	$^3J_{NH,\alpha}$ - HP21	$^3J_{NH,\alpha}$ – peptides[(d)]
L42	0.27	0.09	0.05	6.6	-
S43	0.01	0.04	0.03	-	6.3
D44	-0.30	0.04	0.04	-	5.3
E45	-0.16	0.05	0.05	5.4	5.5
D46	-0.22	0.02	0.00	6.7	6.7
F47	-0.53	0.12	0.09	-	5.6
K48	0.07	0.18	0.20	5.0	6.4
A49	-0.20	-0.04	-0.03	4.9	5.5
V50	-0.49	-0.30	-0.30	7.3	7.4
F51	-0.26	-0.31	-0.14	-	6.8
G52	0.13, -0.06	0.09, 0.07	0.05, 0.03	-	-
M53	0.27	0.15	0.11	4.5	7.3, 7.0
T54	0.29	-0.83	0.16	6.3	7.2
R55	0.23	-0.16	-0.57	4.4	6.8
S56	-0.29	-0.06	-0.02	5.5	6.4
A57	-0.17	-0.03	0.05	5.7	5.8
F58	-0.23	-0.03	0.04	-	7.3
A59	-0.09	-0.39	0.04	4.9	6.1
N60	-0.10	-0.07	-0.02	8.7	7.3
L61	-0.20	-0.05	-0.09	7.0	7.2

[(a)]Calculated using random coil values of Wishart etal.(*1*)

[(b)]Ring current contributions predicted from NMR structure of HP35. pdb code: 1VII

[(c)]Ring current contributions predicted from X-ray structure of HP35. pdb code: 1YRF

[(d)]Coupling constants previously measure for peptides corresponding to Leu42 to Met53 and Gly52 to L61. When two values are given they correspond to the values measured in both peptides (*2*).

Table III

Calculated intrinsic exchange rates for an unstructured polypeptide with the sequence of HP21 at 5.0 ^{o}C, pD_{corr} = 5.40. The calculated time constants and halflifes are included. Calculations were performed using the SPHERE program of Roder and colleagues (http://www.fccc.edu/research/labs/roder/sphere).

Residue	K_{ex} (sec^{-1})	Time Const. (min.)	HalfLife (min.)
L42	1.15E-01	0.14	0.10
S43	1.20E-02	1.38	0.96
D44	1.08E-02	1.55	1.07
E45	2.64E-03	6.32	4.38
D46	4.49E-03	3.71	2.57
F47	3.98E-03	4.19	2.90
K48	8.76E-03	1.90	1.32
A49	1.10E-02	1.52	1.05
V50	1.80E-03	9.27	6.43
F51	3.58E-03	4.65	3.22
G52	1.77E-02	0.94	0.65
M53	1.20E-02	1.38	0.96
T54	9.17E-03	1.82	1.26
R55	1.58E-02	1.05	0.73
S56	3.21E-02	0.52	0.36
A57	1.66E-02	1.01	0.70
F58	4.89E-03	3.41	2.36
A59	9.59E-03	1.74	1.20
N60	2.56E-02	0.65	0.45
L61	2.37E-04	70.2	48.7

References:

(1) Wishart, D. S., Bigam, C. G., Holm, A., Hodges, R. S., and Sykes, B. D. (1995) ^{1}H, ^{13}C and ^{15}N random coil NMR chemical shifts of the common amino acids. I. Investigations of nearest-neighbor effects. *J. Biomol. NMR 5*, 67-81.

(2) Tang, Y. F., Rigotti, D. J., Fairman, R., and Raleigh, D. P. (2004) Peptide models provide evidence for significant structure in the denatured state of a rapidly folding protein: The villin headpiece subdomain. *Biochemistry 43*, 3264-72.