Supplementary Material

Table S1: Comparison of bond topological properties in the main chain of eight tripeptides derived from experiment, units: $[\varrho_{bcp}]$=1 eÅ^{-3}, $[\nabla^2\varrho_{bcp}]$=1 eÅ^{-5}

bond type	bond	AHA		AFA		AAA [1]		AYA [2]		APA		AGA	
		ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$
N_{amm}-C_α	N1-C1	1.56(2)	-9.4(1)	1.80(2)	-11.1(8)	1.83(4)	-14.2(2)	1.70(3)	-8.9(1)	1.75(2)	-9.9(1)	1.79(3)	-11.3(1)
						1.69(4)	-8.3(2)	1.71(3)	-9.3(1)				
(N_{amm}-)C_α-C_{pep}	C1-C2	1.65(2)	-10.2(4)	1.74(2)	-13.3(1)	1.74(4)	-11.3(2)	1.67(3)	-8.9(1)	1.75(1)	-12.1(1)	1.74(3)	-10.0(1)
						1.76(4)	-11.7(2)	1.75(3)	-13.6(1)				
(N_{pep}-)C_α-C_{pep}	C3-C4	1.70(2)	-11.5(7)	1.73(2)	-11.5(1)	1.64(4)	-9.0(2)	1.64(3)	-7.8(1)	1.74(1)	-11.2(1)	1.78(4)	-12.8(1)
						1.72(4)	-13.1(2)	1.76(3)	-12.9(1)				
(N_{amm}-C_α-)C_{pep}-O_{pep}	C2-O1	2.84(4)	-36.6(2)	2.80(3)	-29.1(2)	2.92(5)	-30.4(3)	2.95(4)	-25.6(2)	2.96(2)	-31.4(2)	3.00(5)	-35.3(3)
						2.82(5)	-24.5(3)	2.83(5)	-35.7(3)				
(N_{pep}-C_α-)C_{pep}-O_{pep}	C4-O2	2.66(4)	-27.0(3)	2.75(3)	-24.4(2)	2.88(5)	-32.4(3)	2.99(4)	-28.8(3)	2.90(2)	-31.8(2)	2.95(5)	-33.8(3)
						2.86(5)	-30.5(3)	2.98(5)	-42.8(3)				
(N_{amm}-C_α-)C_{pep}-N_{pep}	C2-N2	2.43(3)	-28.2(2)	2.45(2)	-23.4(1)	2.39(4)	-23.3(2)	2.44(4)	-20.6(2)	2.43(2)	-22.1(1)	2.49(4)	-20.5(2)
						2.43(4)	-21.9(2)	2.43(3)	-24.4(2)				
(N_{pep}-C_α-)C_{pep}-N_{pep}	C4-N3	2.30(3)	-29.2(2)	2.44(3)	-22.8(1)	2.43(4)	-22.0(2)	2.39(4)	-19.2(2)	2.45(2)	-23.1(1)	2.51(3)	-20.9(2)
						2.45(4)	-24.8(2)	2.53(3)	-27.0(2)				
N_{pep}-C_α(-C_{pep})	N2-C3	1.67(2)	-7.8(1)	1.80(2)	-12.3(9)	1.82(4)	-9.4(2)	1.75(3)	-9.4(1)	1.81(2)	-11.6(1)	1.94(4)	-15.2(2)
						1.88(4)	-13.2(2)	1.84(3)	-12.5(1)				
N_{pep}-C_α(-C_{carbox})	N3-C5	1.72(3)	-14.0(1)	1.85(2)	-13.0(1)	1.80(4)	-10.7(2)	1.81(3)	-9.6(1)	1.87(2)	-11.9(1)	1.85(5)	-12.3(2)
						1.80(4)	-10.9(2)	1.88(3)	-14.4(1)				
C_α-C_{carbox}	C5-C6	1.62(2)	-11.1(7)	1.69(2)	-10.3(1)	1.79(4)	-11.5(2)	1.59(3)	-6.7(1)	1.72(1)	-12.2(1)	1.79(3)	-10.7(1)
						1.77(4)	-10.9(2)	1.77(3)	-14.2(1)				
C_{carbox}-O_{carbox} (short)	C6-O3	2.58(4)	-31.7(2)	2.61(4)	-37.2(3)	2.82(5)	-32.6(3)	2.97(4)	-34.5(3)	2.79(3)	-30.0(2)	2.88(6)	-34.9(3)
						2.82(5)	-33.5(3)	2.81(4)	-30.1(3)				
C_{carbox}-O_{carbox} (long)	C6-O4	2.62(4)	-34.0(3)	2.66(3)	-31.0(2)	2.76(5)	-30.6(3)	2.64(4)	-24.1(2)	2.73(2)	-29.2(2)	2.81(6)	-31.9(3)
						2.67(5)	-25.3(3)	2.75(4)	-34.7(2)				

[1] first/ second line: two independent molecules in the asymmetric unit; [2] first/ second line: two modifications (AYA·EtOH/ AYA·H_2O); considered equal in nearest neighbor approximation: C1-C2=C3-C4, C2-O1=C4-O2, C2-N2=C4-N3, N2-C3=N3-C5, C6-O3=C6-O4

Table S2: Mean values and standard deviations of bond topological properties in nearest neighbor approximation in the main chain from eight tripeptides AHA, AFA, two independent molecules in the asymmetric unit of AAA, two modifications of AYA, APA and AGA derived from experiment; units: $[\varrho_{bcp}]$=1 eÅ^{-3}, $[\nabla^2\varrho_{bcp}]$=1 eÅ^{-5}

bond type	bond	$\overline{\varrho_{bcp}}$	$\sigma(\varrho_{bcp})$	$\overline{\nabla^2\varrho_{bcp}}$	$\sigma(\nabla^2\varrho_{bcp})$
N_{amm}-C_α	N1-C1	1.73	0.09	-10.3	1.9
C_α-C_{pep}	C1-C2 and C3-C4	1.72	0.05	-11.3	1.7
C_{pep}-O_{pep}	C2-O1 and C4-O2	2.88	0.10	-31.3	4.9
C_{pep}-N_{pep}	C2-N2 [1] and C4-N3	2.44	0.05	-23.3	2.8
N_{pep}-C_α	N2-C3 [1] and N3-C5	1.82	0.07	-11.8	2.0
C_α-C_{carbox}	C5-C6	1.72	0.08	-11.0	2.1
C_{carbox}-O_{carbox}	C6-O3 and C6-O4	2.75	0.11	-31.6	3.5
			$\overline{\sigma}_{trans,exp}(\varrho_{bcp})$=0.08		$\overline{\sigma}_{trans,exp}(\nabla^2\varrho_{bcp})$=2.7

[1] Bonds in APA that incorporate N2 are left out because N2 is in a different chemical environment.

Table S3: Comparison of atomic properties in the main chain of eight tripeptides derived from experiment, units: [V_{001}]=1 Å^3, [Q_{001}]=1 e

atom type	atom label	AHA		AFA		AAA [1]		AYA [2]		APA		AGA	
		V_{001}	Q_{001}	V_{001}	Q_{001}	V_{001}	Q_{001}	V_{001}	Q_{001}	V_{001}	Q_{001}	V_{001}	Q_{001}
N_{amm}	N1	14.3	-1.14	15.0	-1.33	13.9	-1.12	16.3	-1.51	11.8	-0.97	14.8	-1.38
						14.8	-1.34	14.2	-1.46				
(N_{amm}-)C_α	C1	7.3	0.14	6.6	0.29	7.3	0.07	6.7	0.24	6.9	0.15	6.8	0.18
						7.3	0.04	7.0	0.18				
(N_{pep}-)C_α(-C_{pep})	C3	6.8	0.10	6.6	0.22	7.0	0.17	6.5	0.25	6.6	0.24	8.5	0.14
						6.8	0.27	7.3	0.09				
C_α(-C_{carbox})	C5	6.6	0.50	6.9	0.24	7.1	0.21	7.0	0.26	7.0	0.24	6.9	0.18
						6.8	0.22	7.5	0.14				
(N_{amm}-C_α-)C_{pep}	C2	6.2	1.00	5.9	1.09	5.8	1.05	6.6	0.88	6.1	0.97	5.6	1.09
						5.9	1.05	6.6	1.01				
(N_{pep}-C_α-)C_{pep}	C4	6.3	1.33	5.8	1.09	6.0	1.11	6.8	0.83	6.0	1.02	6.5	0.91
						5.9	1.14	6.6	1.04				
(N_{amm}-C_α-C_{pep}-)O_{pep}	O1	15.9	-0.85	15.3	-1.07	16.2	-1.09	15.9	-1.06	17.9	-1.01	16.5	-1.13
						15.9	-1.15	15.7	-0.93				
(N_{pep}-C_α-C_{pep}-)O_{pep}	O2	17.4	-0.90	16.4	-1.02	16.0	-1.09	16.1	-0.99	17.2	-1.05	14.8	-1.01
						16.0	-1.13	14.4	-1.09				
N_{pep}(-C_α-C_{pep})	N2	13.4	-1.13	13.2	-1.10	12.5	-1.04	12.5	-0.93	10.7	-0.93	13.4	-1.14
						12.8	-1.00	12.5	-1.09				
N_{pep}(-C_α-C_{carbox})	N3	12.9	-0.92	12.3	-1.18	12.6	-1.06	12.2	-0.91	12.7	-0.95	13.7	-1.11
						12.6	-1.02	12.8	-1.03				
C_{carbox}	C6	5.8	1.47	6.1	1.29	6.1	1.13	5.1	1.36	5.6	1.27	5.7	1.26
						5.7	1.23	6.4	1.23				
O_{carbox} (in shorter bond)	O3	15.7	-0.86	17.8	-1.07	16.5	-1.01	16.0	-1.09	15.4	-1.06	16.7	-1.04
						16.5	-0.96	16.5	-1.04				
O_{carbox} (in longer bond)	O4	15.3	-0.81	15.3	-1.02	15.3	-1.03	14.8	-0.96	16.1	-1.11	15.3	-1.06
						14.8	-0.98	16.6	-1.04				

[1] first/ second line: two independent molecules in the asymmetric unit; [2] first/ second line: two modifications (AYA·EtOH/ AYA·H_2O); considered equal in nearest neighbor approximation: C1=C3=C5, C2=C4, O1=O2, N2=N3, O3=O4

Table S4: Mean values and standard deviations of atomic properties in nearest neighbor approximation in the main chain from eight tripeptides AHA, AFA, two independent molecules in the asymmetric unit of AAA, two modifications of AYA, APA and AGA derived from experiment; units: [V_{001}]=1 Å^3, [Q_{001}]=1 e

atom type	atom	$\overline{V_{001}}$	$\sigma(V_{001})$	$\overline{Q_{001}}$	$\sigma(Q_{001})$
N_{amm}	N1	14.4	1.3	-1.28	0.19
C_{α}	C1, C3 and C5	7.0	0.4	0.20	0.09
C_{pep}	C2 and C4	6.2	0.4	1.04	0.12
O_{pep}	O1 and O2	16.1	0.9	-1.04	0.09
N_{pep}[1]	N2 and N3	12.8	0.4	-1.03	0.09
C_{carbox}	C6	5.8	0.4	1.28	0.10
O_{carbox}	O3 and O4	15.9	0.8	-1.01	0.08
			$\overline{\sigma}_{trans,exp}(V_{001})$=0.7		$\overline{\sigma}_{trans,exp}(Q_{001})$=0.11

[1] N2 in APA left out because it is in a different chemical environment.

Table S5a: Comparison of bond topological properties in the main chain of 20 tripeptides of the type AXA derived from theory (AMBER optimization, wavefunction at B3LYP/6-311++g(2d,2p) level of theory), units: $[\varrho_{bcp}]$=1 eÅ^{-3}, $[\nabla^2\varrho_{bcp}]$=1 eÅ^{-5}

bond type	bond	AAA		ACA		ADA		AEA		AFA	
		ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$
N_{amm}-C_α	N1-C1	1.6367	-14.573	1.6375	-14.596	1.6376	-14.597	1.6379	-14.603	1.6386	-14.635
(N_{amm}-)C_α-C_{pep}	C1-C2	1.6855	-13.445	1.6868	-13.465	1.6884	-13.507	1.6874	-13.482	1.6888	-13.526
(N_{pep}-)C_α-C_{pep}	C3-C4	1.6747	-13.246	1.6738	-13.201	1.6721	-13.211	1.6730	-13.209	1.6730	-13.215
(N_{amm}-C_α-)C_{pep}-O_{pep}	C2-O1	2.7475	-18.478	2.7509	-18.633	2.7507	-18.655	2.7482	-18.516	2.7485	-18.544
(N_{pep}-C_α-)C_{pep}-O_{pep}	C4-O2	2.7340	-17.803	2.7353	-17.857	2.7354	-17.849	2.7352	-17.854	2.7344	-17.797
(N_{amm}-C_α-)C_{pep}-N_{pep}	C2-N2	2.2945	-26.628	2.2906	-26.636	2.2909	-26.626	2.2927	-26.623	2.2909	-26.628
(N_{pep}-C_α-)C_{pep}-N_{pep}	C4-N3	2.2979	-26.620	2.2982	-26.590	2.2996	-26.576	2.2984	-26.599	2.2992	-26.606
N_{pep}-C_α(-C_{pep})	N2-C3	1.7046	-15.927	1.7035	-15.848	1.7098	-15.946	1.7001	-15.779	1.7061	-15.873
N_{pep}-C_α(-C_{carbox})	N3-C5	1.6911	-15.548	1.6890	-15.491	1.6876	-15.457	1.6894	-15.501	1.6879	-15.466
C_α-C_{carbox}	C5-C6	1.6785	-13.378	1.6776	-13.364	1.6767	-13.353	1.6776	-13.365	1.6769	-13.357
C_{carbox}-O_{carbox} (short)	C6-O3	2.6305	-19.051	2.6309	-19.085	2.6310	-19.102	2.6312	-19.127	2.6320	-19.271
C_{carbox}-O_{carbox} (long)	C6-O4	2.6182	-18.873	2.6186	-18.885	2.6192	-18.924	2.6183	-18.863	2.6180	-18.822

considered equal in nearest neighbor approximation: C1-C2=C3-C4, C2-O1=C4-O2, C2-N2=C4-N3, N2-C3=N3-C5, C6-O3=C6-O4

Table S5b: Comparison of bond topological properties in the main chain of 20 tripeptides of the type AXA derived from theory (AMBER optimization, wavefunction at B3LYP/6-311++g(2d,2p) level of theory), units: $[\varrho_{bcp}]$=1 eÅ^{-3}, $[\nabla^2\varrho_{bcp}]$=1 eÅ^{-5}

bond type	bond	AGA		AHA		AIA		AKA		ALA	
		ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$
N_{amm}-C_α	N1-C1	1.6384	-14.630	1.6358	-14.544	1.6355	-14.540	1.6364	-14.559	1.6364	-14.559
(N_{amm}-)C_α-C_{pep}	C1-C2	1.6845	-13.432	1.6884	-13.511	1.6866	-13.471	1.6867	-13.471	1.6870	-13.477
(N_{pep}-)C_α-C_{pep}	C3-C4	1.6651	-13.157	1.6741	-13.231	1.6710	-13.135	1.6751	-13.225	1.6736	-13.190
(N_{amm}-C_α-)C_{pep}-O_{pep}	C2-O1	2.7471	-18.378	2.7497	-18.609	2.7477	-18.462	2.7478	-18.496	2.7491	-18.447
(N_{pep}-C_α-)C_{pep}-O_{pep}	C4-O2	2.7362	-17.987	2.7341	-17.775	2.7352	-17.747	2.7341	-17.790	2.7339	-17.787
(N_{amm}-C_α-)C_{pep}-N_{pep}	C2-N2	2.3015	-26.818	2.2916	-26.650	2.2928	-26.590	2.2930	-26.609	2.2937	-26.618
(N_{pep}-C_α-)C_{pep}-N_{pep}	C4-N3	2.3047	-26.735	2.2983	-26.609	2.2957	-26.604	2.2971	-26.619	2.2973	-26.622
N_{pep}-C_α(-C_{pep})	N2-C3	1.7149	-16.122	1.7033	-15.820	1.6900	-15.537	1.6961	-15.715	1.6954	-15.698
N_{pep}-C_α(-C_{carbox})	N3-C5	1.6863	-15.459	1.6923	-15.571	1.6969	-15.649	1.6927	-15.579	1.6927	-15.578
C_α-C_{carbox}	C5-C6	1.6786	-13.383	1.6786	-13.380	1.6785	-13.381	1.6788	-13.382	1.6788	-13.382
C_{carbox}-O_{carbox} (short)	C6-O3	2.6308	-19.109	2.6300	-19.011	2.6311	-19.137	2.6305	-19.048	2.6305	-19.056
C_{carbox}-O_{carbox} (long)	C6-O4	2.6182	-18.840	2.6185	-18.895	2.6179	-18.807	2.6180	-18.852	2.6179	-18.852

considered equal in nearest neighbor approximation: C1-C2=C3-C4, C2-O1=C4-O2, C2-N2=C4-N3, N2-C3=N3-C5, C6-O3=C6-O4

Table S5c: Comparison of bond topological properties in the main chain of 20 tripeptides of the type AXA derived from theory (AMBER optimization, wavefunction at B3LYP/6-311++g(2d,2p) level of theory), units: $[\varrho_{bcp}]$=1 eÅ^{-3}, $[\nabla^2\varrho_{bcp}]$=1 eÅ^{-5}

bond type	bond	AMA		ANA		APA		AQA		ARA	
		ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$
N_{amm}-C_α	N1-C1	1.6366	-14.570	1.6373	-14.584	1.6317	-14.381	1.6373	-14.592	1.6376	-14.597
(N_{amm}-)C_α-C_{pep}	C1-C2	1.6861	-13.465	1.6877	-13.490	1.6579	-12.907	1.6873	-13.483	1.6873	-13.481
(N_{pep}-)C_α-C_{pep}	C3-C4	1.6601	-12.992	1.6738	-13.228	1.6639	-13.030	1.6734	-13.211	1.6745	-13.226
(N_{amm}-C_α-)C_{pep}-O_{pep}	C2-O1	2.7472	-18.444	2.7522	-18.722	2.7472	-18.342	2.7477	-18.489	2.7484	-18.529
(N_{pep}-C_α-)C_{pep}-O_{pep}	C4-O2	2.7359	-18.023	2.7345	-17.793	2.7357	-17.916	2.7352	-17.856	2.7345	-17.813
(N_{amm}-C_α-)C_{pep}-N_{pep}	C2-N2	2.2963	-26.666	2.2900	-26.634	2.2377	-25.411	2.2932	-26.621	2.2923	-26.618
(N_{pep}-C_α-)C_{pep}-N_{pep}	C4-N3	2.2990	-26.635	2.2989	-26.592	2.3000	-26.746	2.2981	-26.607	2.2982	-26.604
N_{pep}-C_α(-C_{pep})	N2-C3	1.7076	-15.885	1.7061	-15.888	1.7160	-15.643	1.6994	-15.769	1.6993	-15.766
N_{pep}-C_α(-C_{carbox})	N3-C5	1.6882	-15.491	1.6903	-15.523	1.6979	-15.700	1.6892	-15.497	1.6898	-15.510
C_α-C_{carbox}	C5-C6	1.6790	-13.385	1.6780	-13.369	1.6818	-13.427	1.6775	-13.365	1.6778	-13.368
C_{carbox}-O_{carbox} (short)	C6-O3	2.6304	-19.044	2.6301	-18.991	2.6297	-18.996	2.6317	-19.194	2.6311	-19.124
C_{carbox}-O_{carbox} (long)	C6-O4	2.6179	-18.855	2.6191	-18.936	2.6167	-18.730	2.6178	-18.824	2.6184	-18.869

considered equal in nearest neighbor approximation: C1-C2=C3-C4, C2-O1=C4-O2, C2-N2=C4-N3, N2-C3=N3-C5, C6-O3=C6-O4

Table S5d: Comparison of bond topological properties in the main chain of 20 tripeptides of the type AXA derived from theory (AMBER optimization, wavefunction at B3LYP/6-311++g(2d,2p) level of theory), units: $[\varrho_{bcp}]$=1 eÅ^{-3}, $[\nabla^2\varrho_{bcp}]$=1 eÅ^{-5}

bond type	bond	ASA		ATA		AVA		AWA		AYA	
		ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$
N_{amm}-C_α	N1-C1	1.6366	-14.570	1.6358	-14.549	1.6359	-14.550	1.6359	-14.549	1.6390	-14.646
(N_{amm}-)C_α-C_{pep}	C1-C2	1.6861	-13.465	1.6869	-13.482	1.6865	-13.466	1.6888	-13.526	1.6890	-13.530
(N_{pep}-)C_α-C_{pep}	C3-C4	1.6601	-12.992	1.6634	-12.972	1.6717	-13.154	1.6742	-13.234	1.6732	-13.215
(N_{amm}-C_α-)C_{pep}-O_{pep}	C2-O1	2.7472	-18.444	2.7480	-18.480	2.7478	-18.474	2.7495	-18.597	2.7480	-18.520
(N_{pep}-C_α-)C_{pep}-O_{pep}	C4-O2	2.7359	-18.023	2.7325	-17.758	2.7352	-17.748	2.7343	-17.796	2.7343	-17.791
(N_{amm}-C_α-)C_{pep}-N_{pep}	C2-N2	2.2963	-26.664	2.2933	-26.614	2.2927	-26.589	2.2910	-26.642	2.2910	-26.625
(N_{pep}-C_α-)C_{pep}-N_{pep}	C4-N3	2.2990	-26.635	2.2997	-26.581	2.2960	-26.602	2.2987	-26.628	2.2991	-26.612
N_{pep}-C_α(-C_{pep})	N2-C3	1.7076	-15.885	1.6948	-15.568	1.6921	-15.590	1.7058	-15.862	1.7050	-15.861
N_{pep}-C_α(-C_{carbox})	N3-C5	1.6882	-15.491	1.6865	-15.435	1.6959	-15.629	1.6904	-15.527	1.6882	-15.474
C_α-C_{carbox}	C5-C6	1.6790	-13.385	1.6773	-13.364	1.6784	-13.378	1.6779	-13.369	1.6770	-13.359
C_{carbox}-O_{carbox} (short)	C6-O3	2.6304	-19.044	2.6316	-19.194	2.6310	-19.115	2.6312	-19.153	2.6322	-19.285
C_{carbox}-O_{carbox} (long)	C6-O4	2.6179	-18.855	2.6186	-19.194	2.6181	-18.837	2.6179	-18.839	2.6178	-18.807

considered equal in nearest neighbor approximation: C1-C2=C3-C4, C2-O1=C4-O2, C2-N2=C4-N3, N2-C3=N3-C5, C6-O3=C6-O4

Table S6: Mean values and standard deviations of bond topological properties in nearest neighbor approximation in the main chain from 20 tripeptides of the type AXA derived from theory (AMBER optimization, wavefunction at B3LYP/6-311++g(2d,2p) level of theory); units: $[\varrho_{bcp}]$=1 eÅ^{-3}, $[\nabla^2\varrho_{bcp}]$=1 eÅ^{-5}

bond type	bond	$\overline{\varrho_{bcp}}$	$\sigma(\varrho_{bcp})$	$\overline{\nabla^2\varrho_{bcp}}$	$\sigma(\nabla^2\varrho_{bcp})$
N_{amm}-C_α	N1-C1	1.637	0.002	-14.57	0.05
C_α-C_{pep}	C1-C2 and C3-C4	1.678	0.010	-13.31	0.19
C_{pep}-O_{pep}	C2-O1 and C4-O2	2.742	0.007	-18.18	0.35
C_{pep}-N_{pep}	C2-N2 [1] and C4-N3	2.296	0.004	-26.63	0.05
N_{pep}-C_α	N2-C3 [1] and N3-C5	1.696	0.008	-15.66	0.18
C_α-C_{carbox}	C5-C6	1.678	0.001	-13.38	0.02
C_{carbox}-O_{carbox}	C6-O3 and C6-O4	2.625	0.007	-18.99	0.15
			$\overline{\sigma}_{trans,theo}(\varrho_{bcp})$=0.005		$\overline{\sigma}_{trans,theo}(\nabla^2\varrho_{bcp})$=0.14

[1] Bonds in APA that incorporate N2 are left out because N2 is in a different chemical environment.

Table S7a: Comparison of atomic properties in the main chain of 20 tripeptides of the type AXA derived from theory (AMBER optimization, wavefunction at B3LYP/6-311++g(2d,2p) level of theory), units: [V_{001}]=1 Å^3, [Q_{001}]=1 e

atom type	atom label	AAA		ACA		ADA		AEA		AFA	
		V_{001}	Q_{001}	V_{001}	Q_{001}	V_{001}	Q_{001}	V_{001}	Q_{001}	V_{001}	Q_{001}
N_{amm}	N1	12.623	-0.9288	12.620	-0.9274	12.739	-0.9353	12.629	-0.9265	12.610	-0.9198
(N_{amm}-)C_α	C1	6.790	0.2799	7.160	0.2613	6.924	0.2806	6.961	0.2805	7.215	0.2713
(N_{pep}-)C_α(-C_{pep})	C3	6.721	0.3280	6.665	0.3194	7.031	0.3116	6.718	0.3191	7.747	0.2851
C_α(-C_{carbox})	C5	6.775	0.3266	6.751	0.3253	6.754	0.3250	6.721	0.3268	6.830	0.3237
(N_{amm}-C_α-)C_{pep}	C2	5.899	1.3428	6.078	1.3072	6.028	1.3110	6.255	1.2962	6.698	1.2946
(N_{pep}-C_α-)C_{pep}	C4	5.853	1.3358	5.821	1.3342	5.858	1.3349	5.798	1.3393	5.829	1.3370
(N_{amm}-C_α-C_{pep}-)O_{pep}	O1	20.092	-1.1245	19.410	-1.1095	19.558	-1.1071	19.625	-1.1193	19.372	-1.1079
(N_{pep}-C_α-C_{pep}-)O_{pep}	O2	20.409	-1.1709	20.357	-1.1662	20.336	-1.1647	20.332	-1.1657	20.382	-1.1682
N_{pep}(-C_α-C_{pep})	N2	13.433	-1.0335	14.517	-1.1079	13.564	-1.0413	14.279	-1.0809	14.194	-1.0311
N_{pep}(-C_α-C_{carbox})	N3	13.366	-1.0274	13.412	-1.0305	13.395	-1.0282	13.350	-1.0262	13.394	-1.0280
C_{carbox}	C6	5.192	1.6234	5.179	1.6230	5.123	1.6285	5.191	1.6247	5.154	1.6261
O_{carbox} (in shorter bond)	O3	21.960	-1.1855	21.987	-1.1851	21.988	-1.1878	21.968	-1.1897	22.157	-1.2044
O_{carbox} (in longer bond)	O4	21.765	-1.2203	21.745	-1.2184	21.748	-1.2196	21.810	-1.2202	21.791	-1.2231

considered equal in nearest neighbor approximation: C1=C3=C5, C2=C4, O1=O2, N2=N3, O3=O4

Table S7b: Comparison of atomic properties in the main chain of 20 tripeptides of the type AXA derived from theory (AMBER optimization, wavefunction at B3LYP/6-311++g(2d,2p) level of theory), units: [V_{001}]=1 Å^3, [Q_{001}]=1 e

atom type	atom label	AGA		AHA		AIA		AKA		ALA	
		V_{001}	Q_{001}	V_{001}	Q_{001}	V_{001}	Q_{001}	V_{001}	Q_{001}	V_{001}	Q_{001}
N_{amm}	N1	12.612	-0.9264	12.712	-0.9250	12.573	-0.9251	12.730	-0.9284	12.613	-0.9244
(N_{amm}-)C_α	C1	6.904	0.2824	7.154	0.2748	6.896	0.2822	6.932	0.2806	6.815	0.2740
(N_{pep}-)C_α(-C_{pep})	C3	8.054	0.3239	7.353	0.2865	7.230	0.2916	6.760	0.3121	7.015	0.2935
C_α(-C_{carbox})	C5	6.716	0.3270	6.742	0.3261	6.791	0.3238	6.704	0.3291	6.801	0.3285
(N_{amm}-C_α-)C_{pep}	C2	5.826	1.3454	5.806	1.3213	6.072	1.3027	6.050	1.3283	5.912	1.3184
(N_{pep}-C_α-)C_{pep}	C4	6.100	1.3426	5.850	1.3369	5.717	1.3298	5.773	1.3375	5.817	1.3405
(N_{amm}-C_α-C_{pep}-)O_{pep}	O1	20.218	-1.1217	19.503	-1.1094	19.877	-1.1216	19.598	-1.1185	19.587	-1.1123
(N_{pep}-C_α-C_{pep}-)O_{pep}	O2	20.381	-1.1693	20.332	-1.1690	20.330	-1.1688	20.394	-1.1703	20.309	-1.1717
N_{pep}(-C_α-C_{pep})	N2	13.990	-1.0434	13.044	-1.0304	14.136	-1.0767	15.185	-1.1439	14.187	-1.0498
N_{pep}(-C_α-C_{carbox})	N3	13.372	-1.0238	13.387	-1.0285	13.321	-1.0353	13.456	-1.0330	13.391	-1.0301
C_{carbox}	C6	5.136	1.6270	5.133	1.6268	5.166	1.6276	5.157	1.6257	5.180	1.6325
O_{carbox} (in shorter bond)	O3	21.990	-1.1877	21.988	-1.1850	22.289	-1.1917	22.117	-1.1879	22.275	-1.2000
O_{carbox} (in longer bond)	O4	21.759	-1.2185	21.757	-1.2173	21.784	-1.2219	21.815	-1.2200	21.883	-1.2274

considered equal in nearest neighbor approximation: C1=C3=C5, C2=C4, O1=O2, N2=N3, O3=O4

Table S7c: Comparison of atomic properties in the main chain of 20 tripeptides of the type AXA derived from theory (AMBER optimization, wavefunction at B3LYP/6-311++g(2d,2p) level of theory), units: [V_{001}]=1 Å^3, [Q_{001}]=1 e

atom type	atom label	AMA		ANA		APA		AQA		ARA	
		V_{001}	Q_{001}	V_{001}	Q_{001}	V_{001}	Q_{001}	V_{001}	Q_{001}	V_{001}	Q_{001}
N_{amm}	N1	12.618	-0.9325	12.640	-0.9243	12.594	-0.9240	12.595	-0.9257	12.739	-0.9255
(N_{amm}-)C_α	C1	7.025	0.2887	6.916	0.2596	7.951	0.2331	6.911	0.2825	6.920	0.2817
(N_{pep}-)C_α(-C_{pep})	C3	7.239	0.2945	6.867	0.3134	8.892	0.2451	6.738	0.3121	6.724	0.3135
C_α(-C_{carbox})	C5	6.871	0.3271	6.841	0.3228	7.139	0.2715	6.766	0.3259	6.742	0.2790
(N_{amm}-C_α-)C_{pep}	C2	6.131	1.3085	6.012	1.3151	5.942	1.3247	6.376	1.2882	6.089	1.3287
(N_{pep}-C_α-)C_{pep}	C4	5.705	1.3325	5.871	1.3331	5.711	1.3445	5.809	1.3378	5.918	1.3262
(N_{amm}-C_α-C_{pep}-)O_{pep}	O1	19.954	-1.1229	19.465	-1.0988	20.142	-1.0988	19.628	-1.1206	19.594	-1.1167
(N_{pep}-C_α-C_{pep}-)O_{pep}	O2	20.381	-1.1728	20.375	-1.1590	20.526	-1.1603	20.332	-1.1654	20.332	-1.1670
N_{pep}(-C_α-C_{pep})	N2	14.179	-1.0875	16.264	-1.2367	10.955	-0.9853	14.154	-1.0751	14.637	-1.1120
N_{pep}(-C_α-C_{carbox})	N3	13.395	-1.0447	13.394	-1.0293	13.508	-1.0298	13.387	-1.0298	13.394	-1.0294
C_{carbox}	C6	5.233	1.6361	5.136	1.6256	5.191	1.6192	5.183	1.6266	5.145	1.6273
O_{carbox} (in shorter bond)	O3	22.303	-1.1900	21.926	-1.1802	21.960	-1.1844	22.078	-1.1915	22.143	-1.1910
O_{carbox} (in longer bond)	O4	21.815	-1.2275	21.685	-1.2134	21.785	-1.2182	21.751	-1.2198	21.799	-1.2226

considered equal in nearest neighbor approximation: C1=C3=C5, C2=C4, O1=O2, N2=N3, O3=O4

Table S7d: Comparison of atomic properties in the main chain of 20 tripeptides of the type AXA derived from theory (AMBER optimization, wavefunction at B3LYP/6-311++g(2d,2p) level of theory), units: [V_{001}]=1 Å^3, [Q_{001}]=1 e

atom type	atom label	ASA		ATA		AVA		AWA		AYA	
		V_{001}	Q_{001}	V_{001}	Q_{001}	V_{001}	Q_{001}	V_{001}	Q_{001}	V_{001}	Q_{001}
N_{amm}	N1	12.626	-0.9298	12.575	-0.9264	12.575	-0.9230	12.738	-0.9209	12.595	-0.9194
(N_{amm}-)C_α	C1	6.879	0.2826	6.873	0.2830	6.839	0.2828	7.136	0.2754	7.290	0.2700
(N_{pep}-)C_α(-C_{pep})	C3	6.782	0.3157	7.455	0.2730	7.797	0.2670	7.804	0.2753	7.373	0.2819
C_α(-C_{carbox})	C5	6.846	0.3235	6.686	0.3267	6.769	0.3232	6.876	0.3223	6.804	0.3256
(N_{amm}-C_α-)C_{pep}	C2	5.850	1.3440	6.200	1.3187	6.130	1.3036	5.902	1.3352	5.905	1.3117
(N_{pep}-C_α-)C_{pep}	C4	5.887	1.3375	6.046	1.2943	5.681	1.3333	5.799	1.3387	5.813	1.3385
(N_{amm}-C_α-C_{pep}-)O_{pep}	O1	20.123	-1.1294	19.647	-1.1212	19.884	-1.1226	18.325	-1.0836	19.146	-1.1057
(N_{pep}-C_α-C_{pep}-)O_{pep}	O2	20.181	-1.1564	20.095	-1.1720	20.354	-1.1688	20.490	-1.1785	20.339	-1.1676
N_{pep}(-C_α-C_{pep})	N2	13.256	-1.0256	14.047	-1.0772	14.175	-1.0650	13.108	-1.0299	13.122	-1.0318
N_{pep}(-C_α-C_{carbox})	N3	13.323	-1.0328	13.238	-1.0302	13.268	-1.0321	13.320	-1.0324	13.370	-1.0323
C_{carbox}	C6	5.151	1.6257	5.118	1.6281	5.167	1.6274	5.187	1.6301	5.149	1.6251
O_{carbox} (in shorter bond)	O3	22.018	-1.1872	22.116	-1.1976	22.289	-1.1910	22.275	-1.1985	22.177	-1.2059
O_{carbox} (in longer bond)	O4	21.791	-1.2231	21.834	-1.2265	21.808	-1.2226	21.821	-1.2281	21.968	-1.2337

considered equal in nearest neighbor approximation: C1=C3=C5, C2=C4, O1=O2, N2=N3, O3=O4

Table S8: Mean values and standard deviations of atomic properties in nearest neighbor approximation in the main chain from 20 tripeptides of the type AXA derived from theory (AMBER optimization, wavefunction at B3LYP/6-311++g(2d,2p) level of theory); units: [V_{001}]=1 Å^3, [Q_{001}]=1 e

atom type	atom	$\overline{V_{001}}$	$\sigma(V_{001})$	$\overline{Q_{001}}$	$\sigma(Q_{001})$
N_{amm}	N1	12.64	0.06	-0.926	0.004
C_{α}	C1, C3 and C5	7.02	0.41	0.298	0.025
C_{pep}	C2 and C4	5.95	0.20	1.326	0.016
O_{pep}	O1 and O2	19.99	0.47	-1.141	0.029
N_{pep}[1]	N2 and N3	13.72	0.65	-1.051	0.042
C_{carbox}	C6	5.16	0.03	1.627	0.004
O_{carbox}	O3 and O4	21.95	0.18	-1.207	0.017
			$\overline{\sigma}_{trans,theo}(V_{001})$=0.29		$\overline{\sigma}_{trans,theo}(Q_{001})$=0.019

[1] N2 in APA left out because it is in a different chemical environment.

Table S9: Comparison of bond topological properties in the main chain of eight tripeptides derived from theory (experimental geometries, wavefunction at B3LYP/6-311++g(2d,2p) level of theory); units: $[\varrho_{bcp}]$= eÅ^{-3}, $[\nabla^2\varrho_{bcp}]$=eÅ^{-5}

bond type	bond	AHA		AFA		AAA [1]		AYA [2]		APA		AGA	
		ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$	ϱ_{bcp}	$\nabla^2\varrho_{bcp}$
N_{amm}-C_α	N1-C1	1.59	-13.6	1.56	-12.8	1.69	-15.1	1.57	-13.2	1.57	-13.4	1.60	-14.0
						1.64	-14.5	1.57	-13.4				
(N_{amm}-)C_α-C_{pep}	C1-C2	1.68	-13.3	1.71	-13.8	1.70	-13.7	1.69	-13.5	1.66	-12.9	1.69	13.5
						1.69	-13.4	1.68	-13.3				
(N_{pep}-)C_α-C_{pep}	C3-C4	1.66	-12.9	1.70	-13.6	1.70	-13.6	1.67	-13.1	1.65	-12.8	1.68	-13.3
						1.70	-13.8	1.67	-13.2				
(N_{amm}-C_α-)C_{pep}-O_{pep}	C2-O1	2.67	-19.7	2.72	-19.1	2.72	-17.9	2.69	-19.4	2.69	-19.3	2.75	-18.4
						2.70	-17.9	2.68	-19.5				
(N_{pep}-C_α-)C_{pep}-O_{pep}	C4-O2	2.68	-19.0	2.70	-18.9	2.69	-18.8	2.68	-19.1	2.65	-18.3	2.67	-18.9
						2.70	-18.6	2.68	-19.0				
(N_{amm}-C_α-)C_{pep}-N_{pep}	C2-N2	2.29	-26.6	2.32	-27.2	2.29	-26.8	2.29	-26.4	2.23	-25.2	2.35	-27.8
						2.32	-27.3	2.29	-26.4				
(N_{pep}-C_α-)C_{pep}-N_{pep}	C4-N3	2.30	-26.8	2.38	-28.4	2.32	-27.4	2.30	-26.8	2.29	-26.3	2.37	-28.1
						2.32	-27.3	2.27	-26.2				
N_{pep}-C_α(-C_{pep})	N2-C3	1.72	-16.1	1.72	-16.1	1.75	-16.6	1.71	-16.0	1.68	-14.7	1.77	-17.2
						1.73	-16.4	1.70	-15.9				
N_{pep}-C_α(-C_{carbox})	N3-C5	1.68	-15.5	1.69	-15.3	1.75	-16.4	1.69	-15.7	1.69	-15.6	1.70	-15.7
						1.73	-16.0	1.70	-15.8				
C_α-C_{carbox}	C5-C6	1.64	-12.5	1.64	-12.6	1.68	-13.3	1.64	-12.5	1.64	-12.5	1.69	-13.4
						1.68	-13.2	1.62	-12.1				
C_{carbox}-O_{carbox} (short)	C6-O3	2.53	-20.5	2.50	-22.2	2.51	-17.6	2.56	-18.7	2.54	-21.8	2.56	-19.9
						2.50	-19.1	2.59	-19.0				
C_{carbox}-O_{carbox} (long)	C6-O4	2.56	-20.8	2.65	-17.5	2.62	-19.4	2.50	-22.5	2.54	-19.8	2.62	-19.5
						2.64	-17.6	2.48	-22.5				

[1] first/ second line: two independent molecules in the asymmetric unit; [2] first/ second line: two modifications (AYA·EtOH/ AYA·H_2O); considered equal in nearest neighbor approximation: C1-C2=C3-C4, C2-O1=C4-O2, C2-N2=C4-N3, N2-C3=N3-C5, C6-O3=C6-O4

Table S10: Mean values and standard deviations of bond topological properties in nearest neighbor approximation in the main chain from eight tripeptides AHA, AFA, two independent molecules in the asymmetric unit of AAA, two modifications of AYA, APA and AGA derived from theory (experimental geometries, wavefunction at B3LYP/6-311++g(2d,2p) level of theory) ; units: $[\varrho_{bcp}]$=1 eÅ^{-3}, $[\nabla^2\varrho_{bcp}]$=1 eÅ^{-5}

bond type	bond	$\overline{\varrho_{bcp}}$	$\sigma(\varrho_{bcp})$	$\overline{\nabla^2\varrho_{bcp}}$	$\sigma(\nabla^2\varrho_{bcp})$
N_{amm}-C_α	N1-C1	1.60	0.04	-13.8	0.7
C_α-C_{pep}	C1-C2 and C3-C4	1.68	0.02	-13.4	0.3
C_{pep}-O_{pep}	C2-O1 and C4-O2	2.69	0.02	-18.9	0.5
C_{pep}-N_{pep}	C2-N2 [1] and C4-N3	2.31	0.03	-27.1	0.7
N_{pep}-C_α	N2-C3 [1] and N3-C5	1.72	0.03	-16.0	0.5
C_α-C_{carbox}	C5-C6	1.65	0.03	-12.8	0.5
C_{carbox}-O_{carbox}	C6-O3 and C6-O4	2.56	0.05	-19.9	1.7
			$\overline{\sigma}_{trans,theoexp}(\varrho_{bcp})$=0.03		$\overline{\sigma}_{trans,theoexp}(\nabla^2\varrho_{bcp})$=0.7

[1] Bonds in APA that incorporate N2 are left out because N2 is in a different chemical environment.

Table S11: Comparison of atomic properties in the main chain of eight tripeptides derived from theory (experimental geometries, wavefunction at B3LYP/6-311++g(2d,2p) level of theory) ; units: $[V_{001}]$=1 Å^3, $[Q_{001}]$=1 e

atom type	atom label	AHA		AFA		AAA [1]		AYA [2]		APA		AGA	
		V_{001}	Q_{001}	V_{001}	Q_{001}	V_{001}	Q_{001}	V_{001}	Q_{001}	V_{001}	Q_{001}	V_{001}	Q_{001}
N_{amm}	N1	12.6	-0.91	12.3	-0.89	12.3	-0.93	12.3	-0.87	12.4	-0.89	12.4	-0.90
						12.3	-0.90	12.3	-0.87				
(N_{amm}-)C_α	C1	7.0	0.26	6.3	0.46	6.9	0.27	7.1	0.26	7.5	0.24	9.7	0.09
						6.9	0.27	7.2	0.26				
(N_{pep}-)C_α(-C_{pep})	C3	6.6	0.32	6.1	0.44	6.7	0.32	6.7	0.32	6.7	0.30	8.1	0.33
						6.8	0.32	6.7	0.32				
C_α(-C_{carbox})	C5	6.8	0.32	6.5	0.40	7.3	0.28	7.0	0.31	9.1	0.15	9.3	0.13
						7.4	0.29	6.9	0.32				
(N_{amm}-C_α-)C_{pep}	C2	5.7	1.31	5.8	1.33	5.7	1.34	5.9	1.31	6.2	1.29	6.1	1.36
						5.7	1.34	5.9	1.31				
(N_{pep}-C_α-)C_{pep}	C4	5.9	1.32	5.5	1.34	5.7	1.35	5.6	1.33	6.1	1.27	6.1	1.32
						5.7	1.35	5.7	1.32				
(N_{amm}-C_α-C_{pep}-)O_{pep}	O1	19.6	-1.09	20.0	-1.09	17.7	-1.14	19.8	-1.09	19.8	-1.10	19.6	-1.12
						17.5	-1.13	19.7	-1.09				
(N_{pep}-C_α-C_{pep}-)O_{pep}	O2	20.1	-1.10	19.9	-1.12	20.1	-1.10	19.5	-1.11	19.0	-1.17	18.7	-1.17
						20.0	-1.11	19.7	-1.11				
N_{pep}(-C_α-C_{pep})	N2	13.0	-1.00	13.1	-1.08	13.2	-1.01	13.0	-1.00	16.8	-1.58	15.7	-1.31
						13.2	-1.01	12.8	-1.00				
N_{pep}(-C_α-C_{carbox})	N3	13.2	-0.99	12.0	-1.09	13.0	-1.05	12.7	-1.00	13.7	-1.02	13.8	-1.05
						13.2	-1.04	12.9	-1.00				
C_{carbox}	C6	5.4	1.57	5.4	1.59	5.3	1.58	5.5	1.56	5.4	1.56	5.4	1.60
						5.1	1.60	5.5	1.56				
O_{carbox} (in shorter bond)	O3	22.7	-1.16	21.4	-1.20	20.6	-1.02	21.2	-1.11	21.4	-1.21	21.5	-1.18
						20.4	-0.96	21.9	-1.18				
O_{carbox} (in longer bond)	O4	22.2	-1.13	22.2	-1.12	17.4	-1.17	19.1	-1.20	22.1	-1.17	21.7	-1.21
						19.1	-1.18	22.0	-1.11				

[1] first/ second line: two independent molecules in the asymmetric unit; [2] first/ second line: two modifications (AYA·EtOH/ AYA·H_2O); considered equal in nearest neighbor approximation: C1=C3=C5, C2=C4, O1=O2, N2=N3, O3=O4

Table S12: Mean values and standard deviations of atomic properties in nearest neighbor approximation in the main chain from eight tripeptides AHA, AFA, two independent molecules in the asymmetric unit of AAA, two modifications of AYA, APA and AGA derived from theory (experimental geometries, wavefunction at B3LYP/6-311++g(2d,2p) level of theory); units: [V_{001}]=1 Å^3, [Q_{001}]=1 e

atom type	atom	$\overline{V_{001}}$	$\sigma(V_{001})$	$\overline{Q_{001}}$	$\sigma(Q_{001})$
N_{amm}	N1	12.4	0.1	-0.90	0.02
C_{α}	C1, C3 and C5	7.2	0.9	0.29	0.08
C_{pep}	C2 and C4	5.8	0.2	1.32	0.02
O_{pep}	O1 and O2	19.4	0.8	-1.12	0.03
N_{pep}[1]	N2 and N3	13.2	0.8	-1.04	0.08
C_{carbox}	C6	5.4	0.1	1.58	0.02
O_{carbox}	O3 and O4	21.1	1.4	-1.14	0.07
			$\overline{\sigma}_{trans,theoexp}(V_{001})$=0.6		$\overline{\sigma}_{trans,theoexp}(Q_{001})$=0.05

[1] N2 in APA left out because it is in a different chemical environment.