Supplementary Material for PCCP

Supplementary material on the manuscript: Conformational Structures and Vibrational Spectra of a Model Tripeptide

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Conformation	δ	ϵ	ζ	ω_0	ϕ_1	ψ_1	ω_1	ϕ_2	ψ_2	ω_2	χ_1	χ_2	DFT	DFT+ZPE
A1aD	92	-92	178	-176	175	175	178	-82	77	-177	32	-39	0.1	0.0
A1bD	86	91	-175	-175	176	175	-179	-83	76	-178	32	-40	0.0	0.1
A1gD	91	177	-179	-177	176	174	180	-83	76	-177	32	-39	1.1	0.1
A1aU	89	-93	177	177	-179	-172	-177	-82	83	-176	-10	29	1.4	1.3
A1gU	90	179	179	177	-178	-172	-176	-83	82	-176	-10	29	2.5	1.6
A1bU	87	92	-178	177	-178	-173	-175	-83	81	-176	-8	28	1.4	1.7
A2aD	95	-89	175	169	60	43	-179	-83	75	-178	32	-40	2.0	1.1
A2bD	87	91	-179	167	59	44	-178	-83	76	-178	32	-40	2.9	1.9
A2gD	91	178	178	167	59	43	-179	-83	76	-178	32	-40	4.1	2.5
A2aU	98	-89	175	165	56	52	-176	-84	79	-176	-8	28	5.8	5.3
A2bU	88	92	180	166	55	51	-175	-84	79	-176	-9	29	5.9	5.8
A2'bD	96	92	-173	-175	-57	-42	-173	-86	75	-174	33	-36	1.9	0.8
A2'aD	91	-92	179	-173	-60	-41	-170	-86	73	-175	34	-37	3.8	2.5
A2'gD	88	179	-179	-172	-60	-41	-170	-86	73	-175	34	-36	4.7	2.7
A2'bU	98	91	-172	-177	-56	-38	180	-80	82	-173	-12	30	1.7	1.8
A2'gU	86	175	-179	-173	-58	-40	-177	-82	79	-172	-9	28	6.3	4.9
A2'aU	93	-93	178	-172	-59	-39	-176	-82	79	-174	-11	30	5.4	5.2
A3gD	79	-176	-179	-165	62	-164	-169	-87	71	-176	34	-37	10.7	10.3
A3bD	89	92	-176	-165	63	-163	-169	-87	72	-176	34	-37	9.9	10.6
A3eD	39	-118	176	-164	60	-163	-169	-87	71	-176	34	-37	11.6	11.4
A3aD	101	-91	-177	-167	66	-164	-167	-87	71	-177	34	-37	11.5	12.1
A3gU	81	-176	-178	-164	60	-165	-179	-82	80	-173	-13	31	13.9	12.9
A3bU	90	93	-176	-164	62	-165	-178	-82	80	-174	-13	31	13.1	12.9
A3'gD	98	173	179	164	-62	163	-179	-84	74	-178	33	-39	10.9	10.4
A3'bD	98	98	179	166	-63	166	-179	-83	77	-178	33	-39	11.8	12.0
A3'cD	134	115	-177	163	-61	167	-179	-83	74	-178	33	-39	11.5	12.3
A3'gU	94	175	180	170	-59	126	173	-79	86	-176	-23	36	13.3	13.2
A3'bU	88	94	-179	173	-61	124	172	-78	87	-176	-23	36	14.0	14.3
A4bD	89	91	-175	-166	-172	50	-177	-82	74	-178	34	-39	11.0	10.5

A4'bD	87	92	-178	169	174	-46	-177	-83	76	-178	30	-39	10.2	9.5
A5aD	87	-95	-178	-173	72	-105	-176	-82	74	-178	35	-39	12.5	13.9
A5bD	88	91	-176	170	68	-109	-175	-82	71	-178	35	-39	13.1	14.2
A5'bD	85	92	180	172	-63	117	-174	-87	76	-177	31	-38	11.5	12.6
A6bD	81	89	-173	-167	-118	52	-179	-81	73	-178	32	-40	10.9	11.3
A6'bD	89	93	-177	171	115	-44	-168	-87	73	-177	33	-36	11.8	12.1
B1bD	96	95	-179	7	174	174	180	-83	77	-178	32	-40	11.5	11.7
B1bU	93	94	-177	-2	-178	-172	-176	-83	82	-176	-8	28	13.1	13.4
B2bD	93	94	-178	-12	60	45	180	-82	76	-178	32	-40	6.2	5.6
B2aD	91	-92	178	-13	61	44	-179	-83	75	-178	32	-39	7.8	7.1
B2gD	72	166	179	-19	62	44	-179	-83	74	-178	32	-40	9.9	8.5
B2bU	90	94	-178	-17	60	53	-177	-83	79	-176	-10	29	9.2	9.6
B2hU	33	168	179	-21	60	53	-177	-83	80	-176	-9	29	11.3	10.8
B2aU	93	-91	178	-17	59	52	-176	-84	79	-176	-8	28	10.6	10.8
B2'bD	90	92	180	10	-61	-38	-168	-85	74	-178	33	-37	9.1	8.2
B2'bU	95	96	177	12	-59	-33	-179	-74	92	-176	-17	34	10.4	10.0
B2'aU	105	-80	176	26	-66	-34	-172	-78	83	-177	-15	33	10.4	10.4
B2'gU	126	128	170	7	-57	-32	178	-73	95	-176	-19	35	11.5	10.9
B3fD	123	-179	179	18	59	-158	-167	-85	77	179	32	-37	20.0	20.2
B3aD	84	-94	178	17	58	-163	-168	-86	75	-178	33	-37	19.6	20.1
B3fU	106	-166	179	20	58	-155	-179	-74	94	-178	-22	38	22.7	22.5
B3bU	107	98	168	14	68	-168	-174	-82	84	-176	-14	31	26.4	26.9
B3'gD	86	-173	179	-18	-57	168	-179	-83	75	-178	33	-39	19.0	18.7
B3'gU	88	179	179	-24	-60	-176	-177	-82	81	-176	-8	28	26.1	25.1
B4'bD	90	91	-175	-14	178	-48	-178	-83	76	-178	30	-39	19.1	18.4
C1dD	36	81	0	-178	176	174	180	-83	74	-176	32	-40	30.3	29.5
IgD	87	-175	-178	-165	-56	-38	-177	-89	6	175	35	-38	2.6	0.2
IaD	89	-94	179	-168	-56	-37	-176	-90	6	175	35	-37	2.0	0.3
IbD	77	92	-172	-165	-56	-37	-177	-88	6	175	34	-37	1.9	0.9
IbU	82	93	-173	-167	-57	-33	180	-72	-14	177	-22	36	2.2	1.0

IgU	85	-175	-178	-167	-56	-33	180	-72	-14	179	-22	36	3.6	1.7
IaU	89	-94	179	-169	-57	-33	180	-72	-14	178	-22	36	3.0	1.8
II'gD	81	-177	179	-169	52	-140	180	-91	13	175	35	-37	11.1	10.9
II'bD	89	93	-177	-169	53	-139	-179	-90	12	175	35	-38	11.7	11.6
II'eD	47	-110	176	-167	51	-141	-179	-89	11	175	35	-38	12.1	12.4
II'gU	83	-175	179	-168	55	-146	176	-73	-6	178	-26	38	14.9	13.6
II'bU	88	93	-178	-168	56	-147	176	-73	-6	178	-26	38	15.5	14.7
K1bD	85	91	-177	-176	176	178	-179	-84	-3	175	31	-40	12.9	11.5
K1gD	90	178	180	-178	176	177	-179	-84	-4	175	31	-40	14.2	11.8

TABLE I: Minimum energy conformations for Z-Aib-Pro-NHMe peptide from DFT calculations [B3LYP/6-311++G(d,p)]: Dihedral angles (in degrees), relative energies without and with zero point energies (in kJ/mol). An and Bn ($n = 1, 2, 2', \ldots$, indicate different Aib orientations) are all trans and cis (Z-Aib) conformations of γ turn structures, respectively. I and II' are β turn structures. a,b,... are different Z-cap orientations. U,D indicate up- and down puckering of the Pro ring.

Conformations	δ	ϵ	ζ	ω_0	ϕ_1	ψ_1	ω_1	ϕ_2	ψ_2	ω_2	χ_1	χ_2	DFT	DFT+ZPE
IbU↔II'bU	80	91	-176	-175	16	-90	-169	-68	-19	178	-11	30	38.3	37.5
IbD↔II'bD	81	91	-174	-172	9	-88	-170	-72	-14	177	33	-40	27.0	26.6
A2'bD↔IbD	89	93	-174	-171	-57	-42	-171	-89	36	175	37	-37	8.1	5.2
A2'aD↔IaD	91	-93	178	-172	-57	-43	-171	-90	38	178	37	-36	9.1	6.6
A2'bU↔IbU	94	92	-172	-169	-56	-43	-175	-86	37	177	-3	24	12.4	9.7
A2'aU↔IaU	90	-93	180	-170	-57	-44	-174	-87	38	-177	-2	23	13.4	10.9
A3bD↔II'bD	89	93	-177	-167	55	-157	-175	-90	37	176	36	-37	14.9	13.4
A3eD↔II'eD	44	-116	178	-163	53	-159	-175	-90	39	177	36	-37	15.4	13.7
A3bU↔II'bU	91	94	-177	-167	55	-158	176	-84	38	178	-13	31	19.3	17.2
A1bD↔A1bU	87	92	-177	179	-179	-179	-175	-87	78	-176	22	-5	4.9	4.8
A2bD↔A2bU	88	91	-179	168	57	45	-174	-88	76	-176	22	-5	9.7	8.5
A2'aD↔A2'aU	90	-93	-179	-171	-57	-46	-177	-85	77	-172	20	-3	8.9	7.6
A2'bD↔A2'bU	96	92	-172	-173	-54	-45	-179	-84	79	-172	21	-5	6.2	5.5
A3bD↔A3bU	89	93	-176	-164	62	-171	-179	-85	77	-174	18	-2	17.4	16.7
IaD↔IaU	90	-93	179	-167	-56	-39	-178	-96	16	175	19	0	8.2	6.4
IbD↔IbU	83	95	-172	-165	-55	-39	-178	-94	15	174	18	0	8.5	6.4
II'bD↔II'bU	90	95	-177	-168	55	-148	172	-95	28	174	16	2	20.8	19.5
A2'bD↔A4'bD	89	91	-172	-165	-148	-44	-168	-88	74	-177	34	-35	30.9	30.6
A1bD↔A4'bD	89	92	180	168	180	-102	-176	-83	75	-178	36	-38	24.6	25.2
A1bD↔A4bD	86	91	-175	-165	180	103	-173	-87	77	-177	31	-38	21.7	22.6
A2bD↔A4bD	89	92	-178	171	142	49	180	-82	77	-178	32	-40	30.1	29.8
A4bD↔A6bD	86	90	-174	-169	-143	51	-178	-82	75	-178	33	-39	12.2	11.6
A4'bD↔A6'bD	87	92	-178	169	142	-46	-170	-86	74	-178	33	-36	13.0	12.4
A3'bD↔A5'bD	86	93	180	168	-60	138	-176	-86	76	-177	32	-38	13.0	13.1
A1bD↔A3'bD	88	93	180	167	-115	167	180	-83	77	-178	33	-39	21.3	21.6
A1bD↔A3bD	85	90	-173	-165	116	-165	-169	-87	73	-177	34	-37	20.1	20.4
A3bD↔A5bD	87	92	-176	-168	62	-129	-171	-83	71	-177	36	-38	14.2	14.2
A3bD↔A3gD	98	133	180	-165	62	-163	-169	-87	72	-176	34	-37	12.3	12.0
A3aD↔A3gD	80	-116	-177	-168	64	-164	-169	-87	73	-176	34	-37	13.0	12.9

A3aD↔A3eD	80	-116	-177	-168	64	-164	-169	-87	73	-176	34	-37	13.0	12.9
A1bD↔B1bD [a]	80	89	179	119	164	159	180	-83	75	-177	33	-39	74.6	72.6
A1bD↔B1bD [b]	86	89	-178	-62	170	159	180	-83	75	-178	33	-39	80.7	78.0
A2bD↔B2bD [a]	77	85	180	60	55	47	-173	-85	72	-178	35	-38	76.9	73.2
A2bD↔B2bD [b]	81	87	-177	-124	67	48	-175	-84	73	-178	34	-37	74.1	71.1
A2bU↔B2bU [a]	77	84	179	59	49	55	-177	-82	80	-176	-10	29	75.4	72.6
A2bU↔B2bU [b]	81	87	-178	-123	61	57	-178	-82	80	-176	-11	30	72.8	70.5
A3aD↔B3aD [a]	97	-89	178	118	83	-158	-170	-87	72	-175	33	-37	70.2	68.9
A3aD↔B3aD [b]	97	-92	179	-58	88	-155	-169	-85	75	-178	32	-37	71.1	69.9
A1bD↔K1bD	84	91	-176	-176	176	176	-177	-86	13	173	34	-41	13.4	11.4

TABLE II: Transition states connecting the conformations for Z-Aib-Pro-NHMe peptide listed in Tab. I: Dihedral angles (in degrees), relative energies without and with zero point energies (in kJ/mol).

Conformation	δ	ϵ	ζ	ω_0	ϕ_1	ψ_1	ω_1	ϕ_2	ψ_2	ω_2	χ_1	χ_2	DFT	DFT+ZPE	ΔE
A1bD_cf	88	91	-176	-174	176	172	175	-75	134	180	31	-38	0.0	0.5	36.5
A1bD_f	88	92	-176	-174	176	171	176	-71	139	180	30	-38	16.5	14.3	20.1
A1bU_cf	86	91	-177	178	-178	-171	178	-70	133	180	-17	34	0.5	1.2	37.4
A1bU_c5	87	92	-178	178	-178	-171	-178	-83	81	-176	-9	29	16.5	14.9	21.4
A2bD_cf	90	93	180	171	59	42	175	-75	135	-179	31	-38	0.4	0.0	39.0
A2aU_ae	95	-89	178	172	56	51	-175	-85	78	-176	-6	27	15.8	14.6	26.6
A2aU_e	94	-90	-179	172	56	51	-175	-84	79	-176	-7	27	21.0	18.6	21.3
A2'aD_d1	92	-91	179	-171	-59	-41	-171	-85	72	-175	34	-36	10.9	9.4	29.4
A2'aD_ae	84	-97	-179	-173	-59	-41	-171	-86	73	-175	34	-36	13.4	11.8	26.9
A2'bD_d3	92	91	-173	-172	-59	-40	-171	-85	73	-175	33	-36	3.3	2.3	35.1
A2'bD_cf	105	98	-174	-176	-58	-41	-178	-92	122	-179	34	-30	3.9	3.7	34.5
A2'bD_d2	92	91	-173	-172	-57	-40	-171	-85	73	-175	33	-36	8.7	7.0	29.7
A2'bD_ae	99	94	-173	-178	-56	-42	-175	-85	78	-174	33	-36	10.5	9.8	27.9
A2'bD_b3	81	92	-172	-177	-60	-41	-168	-88	72	-176	35	-36	12.8	11.5	25.6
A2'gD_ae	86	177	-179	-173	-59	-42	-172	-86	73	-174	34	-36	11.1	8.7	29.4
A2'gD_d1	86	178	-179	-171	-60	-41	-170	-86	72	-175	34	-36	11.9	9.4	29.4
A2'aU_d1	92	-92	180	-171	-58	-39	-177	-81	79	-173	-11	30	12.6	11.3	30.2
A2'aU_ae	84	-97	180	-178	-57	-39	-177	-81	79	-173	-11	30	12.9	12.0	29.0
A2'aU_b1	101	-116	179	-172	-60	-39	-174	-81	80	-175	-12	31	16.9	15.2	25.0
A2'bU_cf	102	98	-173	-175	-58	-39	179	-85	118	-178	-8	28	4.5	4.4	33.7
A2'bU_d3	95	97	-170	-169	-57	-37	-177	-79	78	-174	-12	31	5.0	4.5	33.2
A2'bU_ae	99	93	-173	-179	-55	-38	-179	-80	81	-173	-12	31	9.0	8.9	29.2
A2'bU_d1	89	90	-171	-172	-57	-38	-178	-80	79	-173	-12	31	10.9	9.9	27.4
A2'bU_c4	94	90	-171	-174	-56	-38	180	-81	81	-173	-10	30	11.0	9.9	27.3
A2'bU_c5	97	92	-172	-177	-55	-38	179	-80	82	-173	-11	30	13.7	12.2	24.6
A2'bU_b3	89	89	-168	-176	-54	-40	-179	-81	80	-174	-9	29	14.8	13.2	23.0
A2'bU_e	100	94	-174	180	-55	-38	180	-80	80	-173	-11	30	14.8	13.6	23.5
A2'bU_f	103	96	-173	-178	-58	-40	180	-79	119	-177	-13	31	26.1	23.2	12.1
A2'bU_b7	97	90	-172	-175	-56	-38	-179	-79	81	-174	-12	31	30.7	26.7	7.5

A2'gU_ae	89	180	-179	-177	-57	-40	-178	-82	78	-173	-10	29	11.1	9.4	31.7
A2'gU_d1	86	180	-179	-170	-58	-39	-177	-81	78	-173	-10	29	13.6	11.4	29.3
B2'aU_be	110	-80	177	19	-64	-33	-172	-78	83	-178	-16	33	8.3	8.9	38.7
IaD_d1	88	-94	179	-167	-56	-38	-177	-88	5	175	34	-38	7.1	5.2	31.4
IaD_ae	92	-91	-175	-168	-55	-38	-177	-89	10	174	34	-37	12.3	10.0	26.2
IbD_d1	85	93	-173	-167	-55	-37	-177	-89	9	174	34	-37	6.0	4.8	32.5
IbD_ae	98	102	-177	-169	-55	-37	-177	-89	8	174	34	-37	11.9	9.7	26.6
IgD_d1	84	-176	-178	-165	-56	-38	-177	-88	5	175	34	-37	7.6	4.6	31.5
IgD_ae	86	179	-178	-169	-55	-38	-177	-90	8	175	35	-37	9.2	6.6	29.9
IaU_d1	93	-93	178	-168	-57	-33	180	-72	-13	179	-22	36	7.6	5.8	31.9
IaU_ae	81	-99	-179	-170	-57	-33	-179	-73	-13	178	-21	36	13.0	10.9	26.6
IaU_bf	88	-93	176	-170	-70	-29	-165	-65	-35	-178	-29	38	24.1	22.3	15.4
IbU_d2	80	91	-173	-166	-57	-33	180	-70	-15	178	-24	37	2.3	0.8	36.4
IbU_d1	87	94	-175	-169	-56	-33	180	-73	-11	177	-22	36	6.3	4.6	32.4
IbU_d3	83	86	-169	-176	-55	-32	178	-81	7	177	-16	33	8.3	7.0	30.4
IbU_ae	93	96	-176	-169	-57	-33	180	-72	-13	177	-23	37	12.1	10.3	26.7
IbU_b3	63	82	-171	-170	-58	-33	-179	-72	-15	180	-23	37	13.7	12.4	25.0
IbU_b6	93	108	-174	-172	-68	-30	-165	-65	-34	-178	-30	38	23.6	21.3	15.1
IgU_d1	85	-176	-178	-166	-57	-33	180	-72	-13	178	-22	36	8.6	5.6	31.6
IgU_ae	85	-179	180	-169	-57	-33	-179	-74	-11	178	-20	35	10.1	7.3	30.0
II'bD_ce	89	93	-178	-171	56	-138	180	-89	9	176	35	-37	9.6	10.8	38.7
NbU_de	94	95	180	172	172	-40	-179	-61	134	-177	-26	38	-0.8	-0.4	

TABLE III: Minimum energy conformations of Z-Aib-Pro-NHMe clusters with one methanol molecule from DFT calculations [B3LYP/6-311++G(d,p)]: Dihedral angles (in degrees), and relative energies without and with ZPE corrections and binding energies ΔE (in kJ/mol). The same nomenclature as in Tab. I is used, with additional indication for the methanol H-bonding sites. In cases a, b, c, d methanol acts as a donor, while in e, f methanol is an acceptor

Conformation	δ	ϵ	ζ	ω_0	ϕ_1	ψ_1	ω_1	ϕ_2	ψ_2	ω_2	χ_1	χ_2	DFT	DFT+ZPE	ΔE
A2'aD_ae_d1	82	-98	-179	-172	-60	-41	-171	-85	73	-174	34	-36	10.4	11.0	56.7
A2'bD_ae_d3	92	93	-174	-173	-59	-42	-170	-86	70	-176	34	-36	1.7	3.1	63.5
A2'gD_ae_d1	81	178	180	-173	-59	-42	-172	-85	72	-174	33	-36	7.9	7.6	60.1
A2'aU_ae_d1	83	-98	180	-175	-57	-39	-177	-81	78	-173	-11	30	10.1	11.1	58.6
A2'bU_cmf	104	96	-173	-176	-59	-42	-178	-79	132	179	-12	30	-6.5	-4.3	71.5
A2'bU_ae_d3	91	94	-175	-171	-58	-40	-174	-82	74	-175	-10	29	3.7	5.3	61.3
A2'bU_ae_b3	91	94	-170	178	-54	-40	-177	-82	81	-175	-11	30	12.3	13.6	52.7
A2'gU_ae_d1	92	179	-179	-177	-56	-40	-178	-82	78	-173	-9	29	8.1	8.8	59.9
IaD_ae_d1	83	-98	-176	-168	-55	-38	-177	-88	5	175	34	-38	7.2	7.2	58.1
IbD_ae_d2	94	101	-176	-167	-55	-39	-177	-84	1	175	32	-38	6.0	5.9	59.2
IbD_ae_d1	92	98	-175	-168	-55	-38	-177	-89	10	174	34	-37	6.0	6.5	59.2
IgD_ae_d1	88	179	-178	-168	-55	-38	-177	-88	7	175	34	-38	4.2	3.5	61.7
IaU_ae_d2	81	-98	180	-170	-56	-32	-180	-71	-14	179	-23	37	3.2	3.2	63.1
IaU_ae_d1	81	-99	-179	-169	-57	-33	180	-72	-13	178	-22	36	7.4	7.2	58.9
IbU_dm3	76	84	-170	-172	-56	-32	179	-76	-5	180	-20	35	-8.8	-7.0	74.3
IbU_ae_d2	92	98	-176	-169	-56	-33	180	-71	-14	178	-23	37	2.5	3.3	63.0
IbU_ae_d1	87	94	-175	-169	-56	-33	180	-73	-11	177	-22	36	6.3	6.9	59.1
IbU_e_d1	82	91	-173	-168	-56	-33	180	-71	-12	177	-22	36	10.3	9.8	55.2
IbU_ae_b1	58	82	-172	-172	-57	-34	-178	-74	-14	179	-22	36	13.3	13.6	52.2
IbU_ae_b6	87	92	-174	-179	-66	-34	-162	-73	-19	-178	-26	38	22.6	23.9	42.8
IgU_ae_d2	83	-177	-179	-169	-56	-33	180	-71	-14	179	-23	37	0.0	0.0	66.9
IgU_ae_d1	84	180	180	-169	-56	-33	180	-73	-12	178	-22	35	4.4	3.9	62.5
IgU_bmf	90	-176	-179	-174	-69	-36	-166	-68	-38	-176	-25	37	16.9	16.9	50.0
II'bD_ae_d2	87	90	-173	-169	53	-138	-177	-85	3	176	34	-38	17.2	19.0	57.8
II'bD_ae_d1	88	91	-174	-170	54	-138	-179	-88	9	175	35	-38	18.1	19.9	57.0
II'bU_ae_d2	97	98	-178	-171	55	-146	177	-72	-7	178	-27	38	19.4	20.4	59.4
II'bU_ae_d1	100	101	-179	-171	56	-146	176	-73	-4	178	-26	38	23.9	24.0	55.0

TABLE IV: Same as table III, but for Z-Aib-Pro-NHMe clusters with two methanol molecules