Computed and Experimental Chemical Shift Parameters for Rigid and Flexible YAF Peptides in the Solid State

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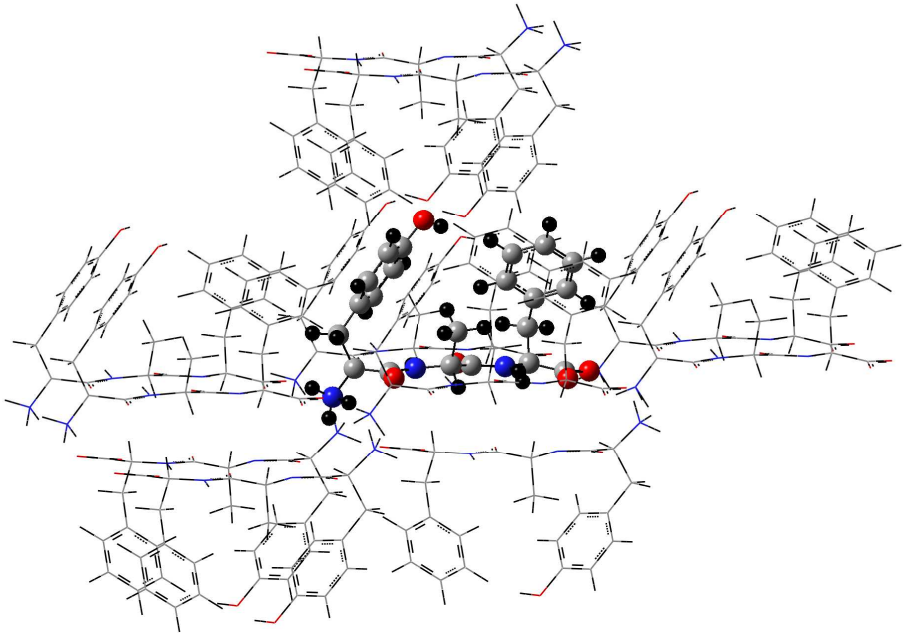

Figure S1. Visualization of cluster (CM calculations) for structure **1**.

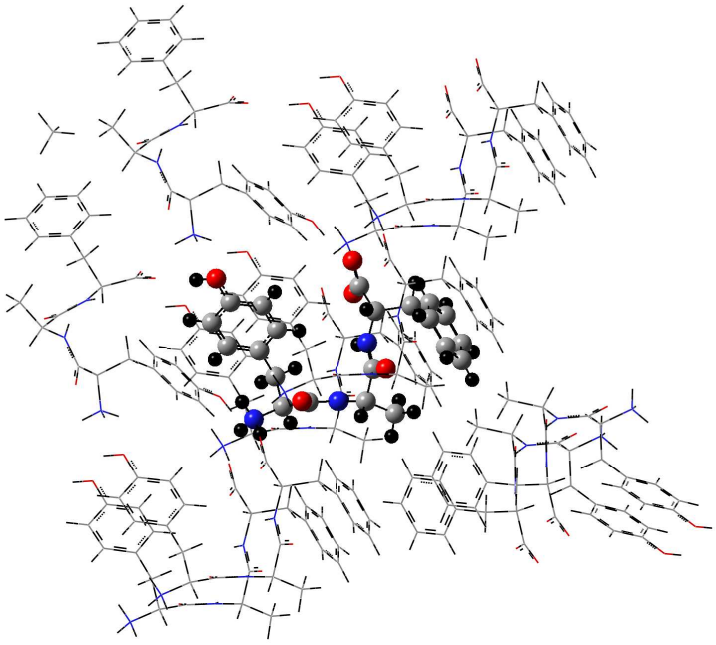

Figure S2. Visualization of cluster (CM calculations) for structure **2a**.

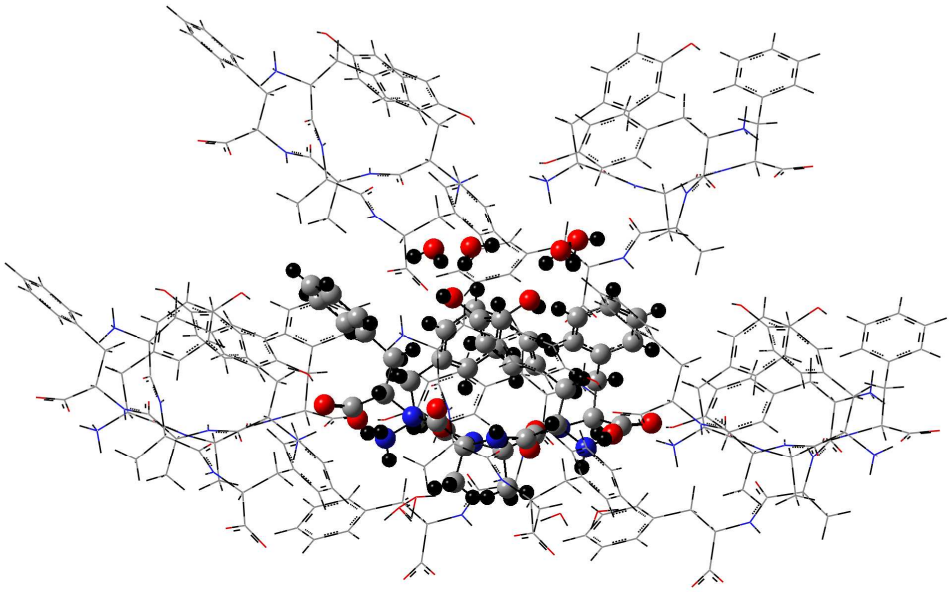

Figure S3. Visualization of cluster (CM calculations) for structure **2b**.

Table S1. Experimental NMR chemical shift tensors [in ppm] for molecular crystal **1**.

Atom	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	Ω^a	κ^b
N-Tyr	26.7	-[c]	-[c]	-[c]	-[c]	-[c]
N-Ala	115.5	220	94	32	188	-0.34
N-Phe	97.1	185	65	42	143	-0.68
C-10	167.2	244	164	94	150	-0.06
C-11	54.1	69	55	38	31	0.09
C-12	37.8	53	39	21	32	0.11
C-13	128.2	221	146	18	203	0.26
C-14	132.1	224	142	31	193	0.15
C-15	115.5	193	128	25	168	0.22
C-16	153.2	239	153	67	172	0.00
C-17	114.9	191	130	24	167	0.27
C-18	129.9	223	148	18	205	0.26
C-20	169.2	246	172	90	156	0.05
C-21	48.2	69	47	29	40	-0.09
C-22	20.3	41	14	6	35	-0.54
C-30	177	237	186	107	130	0.21
C-31	54.1	69	55	38	31	0.09
C-32	34.8	47	38	19	28	0.34
C-33	136.5	233	137	39	194	0.01
C-34	128.8	175	157	54	121	0.70
C-35	126.4	174	157	48	126	0.73
C-36	125.3	222	118	36	186	-0.12
C-37	126.4	174	157	48	126	0.73
C-38	128.8	175	157	54	121	0.70

[a] Span is expressed as: $\Omega = \delta_{11} - \delta_{33}$

[b] Skew is expressed as: $\kappa = (\delta_{22} - \delta_{iso})/\Omega$

[c] Experimental data can not obtained

Table S2. NMR chemical shift tensors [in ppm] for structure **1** (IM methodology) calculated using PBE1PBE functionals with 6-311++G** basis set. Geometry (only hydrogen positions) was optimized with B3LYP functional and 6-311G** basis set. The chemical shifts were calculated from shielding parameters (σ_i) using the equations: $\delta_i = 185.7 - \sigma_i$.(C) and $\delta_i = 220.0 - \sigma_i$.(N).

Atom	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	Ω^a	κ^b
N-Tyr	11.8	31	15	-11	41	0.24
N-Ala	127.1	250	67	64	185	-0.97
N-Phe	114.9	224	65	55	168	-0.89
C-10	160.0	248	142	90	158	-0.34
C-11	52.6	64	55	39	25	0.31
C-12	39.2	63	340	14	49	0.04
C-13	118.5	218	128	10	207	0.13
C-14	134.6	237	142	25	212	0.11
C-15	118.9	206	136	14	192	0.28
C-16	160.2	246	172	62	184	0.19
C-17	117.1	205	12	20	184	0.15
C-18	129.4	234	145	10	224	0.20
C-20	164.1	239	168	86	153	0.07
C-21	49.6	75	49	25	50	-0.03
C-22	17.4	42	12	-1	43	-0.40
C-30	170.4	260	145	106	154	-0.50
C-31	55.4	77	52	37	40	-0.24
C-32	34.4	49	40	13	36	0.51
C-33	143.1	244	179	6	238	0.46
C-34	130.8	239	129	25	214	-0.03
C-35	123.9	232	130	10	222	0.08
C-36	125.0	235	134	7	228	0.11
C-37	129.9	240	142	7	233	0.16
C-38	134.1	238	153	11	228	0.25
RMSD	4.2					

[a] Span is expressed as: $\Omega = \delta_{11} - \delta_{33}$

[b] Skew is expressed as: $\kappa = (\delta_{22} - \delta_{iso})/\Omega$

Table S3. NMR NMR chemical shift tensors [in ppm] for structure **1** (CM, ONIOM methodology) calculated using PBE1PBE functionals with 6-311++G** basis set for high level part of system and molecular mechanics methods with a UFF force field as the low layer. Geometry (only hydrogen positions) was optimized with B3LYP functional and 6-311G** basis set for high level part of system and molecular mechanics methods with a UFF force field as the low layer. The chemical shifts were calculated from shielding parameters (σ_i) using the equations: $\delta_i = 185.4 - \sigma_i$.(C) and $\delta_i = 220.0 - \sigma_i$.(N).

Atom	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	Ω^a	κ^b
N-Tyr	-3.3	29	-13	-26	55	-0.53
N-Ala	129.3	255	69	64	191	-0.95
N-Phe	114.7	223	66	55	168	-0.87
C-10	162.1	247	150	90	157	-0.24
C-11	51.4	65	56	34	31	0.42
C-12	39.5	69	39	11	58	-0.04
C-13	118.6	218	128	11	207	0.13
C-14	134.8	239	141	24	214	0.09
C-15	121.7	211	139	15	196	0.26
C-16	160.2	247	171	62	185	0.18
C-17	118.5	208	130	18	190	0.18
C-18	129.3	238	143	7	231	0.17
C-20	164.1	239	168	85	153	0.08
C-21	49.4	74	49	25	50	-0.02
C-22	17.0	43	11	-3	46	-0.42
C-30	169.9	259	145	106	154	-0.49
C-31	55.3	76	53	37	40	-0.16
C-32	33.2	46	41	12	34	0.69
C-33	142.6	243	180	4	239	0.47
C-34	130.0	238	128	24	213	-0.03
C-35	122.8	231	127	11	220	0.05
C-36	124.5	234	134	6	228	0.12
C-37	129.8	240	143	6	234	0.16
C-38	134.0	240	154	8	231	0.26
RMSD	4.4					

[a] Span is expressed as: $\Omega = \delta_{11} - \delta_{33}$

[b] Skew is expressed as: $\kappa = (\delta_{22} - \delta_{iso})/\Omega$

Table S4. Experimental NMR chemical shift tensors [in ppm] for molecular crystal **2a**.

Atom	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	Ω^a	κ^b
N-Tyr	22.2	-[c]	-[c]	-[c]	-[c]	-[c]
N-Ala	104.7	208	58	48	159	-0.87
N-Phe	101.7	204	55	45	159	-0.87
C-10	169.3	252	167	90	162	-0.04
C-11	53.4	71	57	31	40	0.31
C-12	36.6	45	39	29	19	0.38
C-13	119.6	213	134	12	201	0.21
C-14	131.9	225	143	28	197	0.17
C-15	116.6	189	134	27	162	0.32
C-16	157.2	241	163	67	174	0.10
C-17	113.6	189	126	26	163	0.23
C-18	131.9	225	143	28	197	0.17
C-20	174.8	239	193	91	148	0.37
C-21	54.0	71	57	31	40	0.31
C-22	19.2	31	19	7	24	-0.02
C-30	175.7	247	168	111	136	-0.17
C-31	54.5	71	59	34	37	0.37
C-32	37.5	51	40	21	30	0.28
C-33	136.3	234	163	11	223	0.36
C-34	127.2	224	142	15	209	0.21
C-35	129.3	224	145	18	206	0.23
C-36	125.7	218	146	13	205	0.30
C-37	129.3	224	145	18	206	0.23
C-38	130.9	222	143	27	195	0.19

[a] Span is expressed as: $\Omega = \delta_{11} - \delta_{33}$

[b] Skew is expressed as: $\kappa = (\delta_{22} - \delta_{iso})/\Omega$

[c] Experimental can not obtained

Table S5. NMR NMR chemical shift tensors [in ppm] for structure **2a** (IM methodology) calculated using PBE1PBE functionals with 6-311++G** basis set. Geometry (only hydrogen positions) was optimized with B3LYP functional and 6-311G** basis set. The chemical shifts were calculated from shielding parameters (σ_i) using the equations: $\delta_i = 204.1 - \sigma_i$.(C) and $\delta_i = 220.0 - \sigma_i$.(N).

Atom	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	Ω^a	κ^b
N-Tyr	10.0	21	11	-2	23	0.13
N-Ala	106.7	217	72	31	186	-0.56
N-Phe	102.3	195	65	47	148	-0.76
C-10	162.2	238	158	90	148	-0.08
C-11	56.7	73	62	35	38	0.41
C-12	42.6	53	43	32	21	0.08
C-13	111.8	205	116	15	191	0.06
C-14	140.9	233	169	20	213	0.40
C-15	119.4	196	143	19	177	0.41
C-16	158.3	240	173	63	177	0.24
C-17	117.1	195	117	40	155	-0.01
C-18	123.5	219	117	35	184	-0.10
C-20	166.0	241	167	90	150	0.03
C-21	60.2	82	58	41	41	-0.19
C-22	26.6	40	30	9	31	0.35
C-30	168.8	245	159	102	143	-0.21
C-31	58.0	72	64	38	34	0.55
C-32	42.6	61	47	20	41	0.34
C-33	138.0	225	175	14	211	0.53
C-34	130.5	231	138	23	208	0.11
C-35	126.6	226	135	19	208	0.12
C-36	122.2	222	132	13	209	0.14
C-37	125.3	224	136	17	207	0.15
C-38	133.5	232	153	16	216	0.27
RMSD	5.4					

[a] Span is expressed as: $\Omega = \delta_{11} - \delta_{33}$

[b] Skew is expressed as: $\kappa = (\delta_{22} - \delta_{iso})/\Omega$

Table S6. NMR NMR chemical shift tensors [in ppm] for structure **2a** (CM, ONIOM methodology) calculated using PBE1PBE functionals with 6-311++G** basis set for high level part of system and molecular mechanics methods with a UFF force field as the low layer. Geometry (only hydrogen positions) was optimized with B3LYP functional and 6-311G** basis set for high level part of system and molecular mechanics methods with a UFF force field as the low layer. The chemical shifts were calculated from shielding parameters (σ_i) using the equations: $\delta_i = 187.4 - \sigma_i$.(C) and $\delta_i = 230.0 - \sigma_i$.(N).

Atom	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	Ω^a	κ^b
N-Tyr	11.0	26	5	2	24	-0.75
N-Ala	106.7	207	76	37	170	-0.54
N-Phe	114.0	219	71	52	167	-0.77
C-10	174.3	266	169	89	177	-0.09
C-11	54.2	71	59	32	39	0.36
C-12	37.4	46	38	28	18	0.04
C-13	111.2	213	115	6	207	0.05
C-14	140.8	240	168	14	226	0.36
C-15	118.7	205	126	25	180	0.12
C-16	159.6	246	174	58	188	0.23
C-17	116.2	199	131	19	180	0.25
C-18	125.2	230	116	30	200	-0.14
C-20	167.2	249	165	88	162	-0.05
C-21	54.5	76	53	35	41	-0.14
C-22	19.2	36	21	1	35	0.16
C-30	171.9	255	161	100	154	-0.22
C-31	52.5	66	60	32	34	0.65
C-32	35.9	53	42	13	40	0.44
C-33	140.0	242	173	5	237	0.42
C-34	132.7	242	137	19	223	0.06
C-35	127.0	235	135	11	224	0.11
C-36	123.1	231	132	6	225	0.12
C-37	125.6	232	137	8	225	0.15
C-38	134.1	240	155	8	232	0.26
RMSD	4.3					

[a] Span is expressed as: $\Omega = \delta_{11} - \delta_{33}$

[b] Skew is expressed as: $\kappa = (\delta_{22} - \delta_{iso})/\Omega$

Table S7. Experimental NMR chemical shift tensors [in ppm] for molecular crystal **2b**.

Atom	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	Ω^a	κ^b
N-Tyr	-[c]	-[c]	-[c]	-[c]	-[c]	-[c]
N-Ala	117.1	235	69	48	186	-0.78
N-Phe	108.5	200	64	62	138	-0.98
C-10	168.1	245	169	90	156	0.02
C-11	57.7	70	63	41	29	0.54
C-12	36.1	53	38	17	35	0.20
C-13	124.5	219	126	29	190	0.02
C-14	130.5	183	156	52	131	0.59
C-15	115.9	149	149	49	100	1.00
C-16	155.2	245	144	77	168	-0.19
C-17	115.9	149	149	49	100	1.00
C-18	130.5	183	156	52	131	0.59
C-20	171.1	244	179	91	153	0.15
C-21	48.3	64	54	27	36	0.45
C-22	21.2	42	21	1	41	-0.03
C-30	176.4	237	186	107	130	0.21
C-31	54.3	68	55	41	27	0.06
C-32	42.3	58	46	23	36	0.30
C-33	138	224	164	26	197	0.39
C-34	130.5	183	156	52	131	0.59
C-35	130.5	183	156	52	131	0.59
C-36	130.5	183	156	52	131	0.59
C-37	130.5	183	156	52	131	0.59
C-38	130.5	183	156	52	131	0.59

[a] Span is expressed as: $\Omega = \delta_{11} - \delta_{33}$

[b] Skew is expressed as: $\kappa = (\delta_{22} - \delta_{iso})/\Omega$

[c] Experimental data can not obtained

Table S8. NMR NMR chemical shift tensors [in ppm] for structure **2b** (IM methodology) calculated using PBE1PBE functionals with 6-311++G** basis set. Geometry (only hydrogen positions) was optimized with B3LYP functional and 6-311G** basis set. The chemical shifts were calculated from shielding parameters (σ_i) using the equations: $\delta_i = 185.6 - \sigma_i$.(C) and $\delta_i = 215.0 - \sigma_i$.(N).

Atom	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	Ω^a	κ^b
N-Tyr	11.3	21	17	-4	25	0.68
N-Ala	112.0	230	61	45	185	-0.83
N-Phe	102.0	207	65	34	173	-0.64
C-10	166.3	248	163	87	161	-0.06
C-11	56.1	65	60	43	22	0.59
C-12	36.2	54	36	19	35	0.02
C-13	124.9	225	141	10	215	0.22
C-14	132.9	238	148	12	225	0.21
C-15	119.9	204	138	18	187	0.29
C-16	156.8	249	160	62	187	0.05
C-17	118.9	204	134	19	186	0.24
C-18	133.0	235	143	21	213	0.14
C-20	169.7	252	169	88	164	-0.01
C-21	46.8	68	48	24	44	0.09
C-22	18.8	41	20	-4	45	0.06
C-30	170.4	255	148	108	147	-0.46
C-31	57.9	76	57	41	35	-0.06
C-32	40.5	57	43	22	36	0.20
C-33	143.2	245	176	8	237	0.42
C-34	131.0	238	140	15	222	0.12
C-35	127.6	237	141	5	231	0.17
C-36	125.1	234	138	4	230	0.17
C-37	128.0	237	140	7	230	0.16
C-38	134.4	241	142	20	221	0.11
RMSD	3.0					

[a] Span is expressed as: $\Omega = \delta_{11} - \delta_{33}$

[b] Skew is expressed as: $\kappa = (\delta_{22} - \delta_{iso})/\Omega$

Table S9. NMR NMR chemical shift tensors [in ppm] for structure **2b** (CM, ONIOM methodology) calculated using PBE1PBE functionals with 6-311++G** basis set for high level part of system and molecular mechanics methods with a UFF force field as the low layer. Geometry (only hydrogen positions) was optimized with B3LYP functional and 6-311G** basis set for high level part of system and molecular mechanics methods with a UFF force field as the low layer. The chemical shifts were calculated from shielding parameters (σ_i) using the equations: $\delta_i = 184.8 - \sigma_i$.(C) and $\delta_i = 215.0 - \sigma_i$.(N).

Atom	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	Ω^a	κ^b
N-Tyr	14.6	25	20	-1	25	0.68
N-Ala	117.8	238	65	50	188	-0.83
N-Phe	108.2	217	70	38	179	-0.65
C-10	172.0	246	168	80	166	-0.07
C-11	54.6	59	49	33	26	-0.64
C-12	39.5	54	33	9	45	-0.44
C-13	124.0	218	133	-1	219	0.12
C-14	134.1	229	146	5	225	0.15
C-15	123.2	203	129	16	187	0.09
C-16	157.3	239	157	53	186	0.00
C-17	113.7	187	128	3	184	0.23
C-18	130.6	224	130	15	210	-0.01
C-20	167.4	243	157	79	164	-0.19
C-21	46.0	58	42	16	42	-0.32
C-22	18.1	33	12	-14	47	-0.41
C-30	171.5	249	142	100	149	-0.60
C-31	56.7	62	46	39	23	-1.40
C-32	42.1	56	38	9	46	-0.24
C-33	140.5	233	166	0	233	0.33
C-34	130.0	231	131	5	225	0.02
C-35	128.1	229	134	-2	231	0.08
C-36	126.7	228	131	-2	230	0.06
C-37	131.2	235	136	0	235	0.06
C-38	131.0	233	122	15	219	-0.12
RMSD	3.0					

[a] Span is expressed as: $\Omega = \delta_{11} - \delta_{33}$

[b] Skew is expressed as: $\kappa = (\delta_{22} - \delta_{iso})/\Omega$