Table S1: Torsional angles and total energy values for backbone and side-chain conformers of $CH_3CO–Leu–NHCH_3$ optimized at RHF/3-21G level of theory. Calculated relative energies ($\Delta E_{rel.}$)[a] and numbering definition of the torsional angles which have been taken into account are also shown.

final geometry	χ_1 (7-8-13-14)	χ_2 (8-13-14-15)	χ_2' (8-13-14-17)	ω_0 (2-3-7-8)	ω_1 (8-9-26-27)	ϕ (3-7-8-9)	ψ (7-8-9-26)	energy (hartree)	$\Delta E_{rel.}$ (kcal.mol^{-1})
α_D (g^+, g^+)	50.09	72.02	-166.47	171.77	-179.89	48.04	42.31	-606.563243654	10.03
α_D (g^+, a)	61.51	135.64	-102.18	173.82	-178.32	44.08	47.42	-606.563530829	9.85
α_D (g^+, g^-)	56.54	-70.17	58.23	173.63	179.67	47.10	39.78	-606.557502704	13.64
α_D (a, g^+)	-161.53	68.77	-170.13	172.80	179.46	60.96	38.58	-606.563549298	9.84
α_D (a, a)	-135.46	175.48	-60.45	173.21	179.43	61.90	38.46	-606.565230347	8.79
α_D (a, g^-)	-134.92	-56.29	69.17	173.15	179.50	61.83	38.61	-606.564345361	9.34
α_D (g^-, g^+)	-75.32	71.49	-167.10	172.61	178.99	66.78	28.61	-606.567093063	7.62
α_D (g^-, a)	-59.69	172.45	-66.06	172.76	179.17	63.98	31.53	-606.569621327	6.03
α_D (g^-, g^-)	-73.70	-60.18	66.45	172.64	179.02	66.16	29.08	-606.565769822	8.45
ε_D (g^+, g^+)	67.53	59.98	-178.03	-163.87	-178.73	58.89	176.39	-606.558290172	13.14
ε_D (g^+, a)	59.83	145.88	-93.51	-169.41	-178.33	44.67	-140.72	-606.557656625	13.54
ε_D (g^+, g^-)	63.31	-72.37	55.14	-164.99	-175.84	47.88	-163.86	-606.551095747	17.66
ε_D (a, g^+)	-166.89	61.25	-177.91	-163.17	179.53	71.08	161.83	-606.561285807	11.26
ε_D (a, a)	-166.81	139.86	-99.28	-162.92	-179.77	72.46	158.66	-606.557340853	13.74
ε_D (a, g^-)						Not found			
ε_D (g^-, g^+)	-72.14	70.77	-167.94	-161.88	179.83	69.54	172.49	-606.563451466	9.90
ε_D (g^-, a)	-50.08	178.55	-59.42	-163.21	-179.55	66.32	-178.79	-606.566585510	7.94
ε_D (g^-, g^-)	-66.79	-56.16	70.48	-161.30	179.87	68.98	172.96	-606.562529150	10.48
γ_D (g^+, g^+)	87.35	90.66	-148.86	173.18	-178.52	65.58	-35.44	-606.565348514	8.71
γ_D (g^+, a)	64.15	140.21	-98.65	174.58	-178.63	55.13	-32.26	-606.563875947	9.64
γ_D (g^+, g^-)	69.23	-74.93	52.00	172.89	177.81	48.79	-12.07	-606.560731919	11.61
γ_D (a, g^+)	177.56	54.34	176.91	174.77	-178.69	74.07	-58.14	-606.575750490	2.19
γ_D (a, a)	-157.72	169.92	-68.17	175.59	-179.17	76.11	-62.18	-606.572917294	3.96
γ_D (a, g^-)	-172.78	-78.94	46.68	174.43	-177.90	74.15	-54.45	-606.572585379	4.17
γ_D (g^-, g^+)	-76.37	69.40	-169.06	175.04	-178.55	75.98	-60.34	-606.571881579	4.61
γ_D (g^-, a)	-60.70	172.55	-65.75	174.94	-178.44	74.59	-58.15	-606.574460722	3.00
γ_D (g^-, g^-)	-71.28	-57.65	68.88	175.10	-178.63	75.88	-59.32	-606.570637436	5.39
δ_D (g^+, g^+)	54.40	100.08	-137.58	172.87	-177.62	169.47	-29.42	-606.562562124	10.46
δ_D (g^+, a)	64.90	166.96	-72.37	172.99	-177.78	179.47	-32.88	-606.562841706	10.29
δ_D (g^+, g^-)	64.64	-61.49	66.99	171.59	179.32	175.60	-20.82	-606.556737980	14.12
δ_D (a, g^+)	174.23	54.39	176.52	174.14	-176.63	-172.10	-46.49	-606.567783134	7.19

final geometry	χ_1 (7-8-13-14)	χ_2 (8-13-14-15)	χ_2' (8-13-14-17)	ω_0 (2-3-7-8)	ω_1 (8-9-26-27)	ϕ (3-7-8-9)	ψ (7-8-9-26)	energy (hartree)	$\Delta E_{rel.}$ (kcal.mol^{-1})
δ_D (a, a)	-164.93	167.18	-70.71	174.56	-177.73	-167.48	-52.74	-606.565673920	8.51
δ_D (a, g$^-$)	-178.14	-80.02	45.67	174.17	-176.65	-168.45	-47.76	-606.564850721	9.03
δ_D (g$^-$, g$^+$)	-58.05	93.91	-144.92	173.93	-179.86	-136.68	-60.25	-606.561922522	10.86
δ_D (g$^-$, a)	-60.85	176.97	-60.84	175.65	179.40	-126.25	-62.32	-606.565725214	8.48
δ_D (g$^-$, g$^-$)	-75.01	-52.59	72.94	173.71	179.49	-130.09	-64.22	-606.561806894	10.94
β_L (g$^+$, g$^+$)	49.94	67.90	-170.02	177.71	178.91	-162.91	170.44	-606.576341766	1.82
β_L (g$^+$, a)	77.18	-178.94	-56.61	178.47	178.23	-162.23	168.95	-606.574973581	2.67
β_L (g$^+$, g$^-$)	59.10	-68.22	59.17	178.11	179.29	-163.86	169.17	-606.571271094	5.00
β_L (a, g$^+$)	-175.75	64.36	-174.74	-179.96	178.21	-162.63	154.26	-606.574789141	2.79
β_L (a, a)	-176.43	144.68	-93.85	-179.85	178.88	-161.08	149.55	-606.571112705	5.10
β_L (a, g$^-$)	-172.61	-74.82	51.64	-178.44	-179.57	-154.04	131.54	-606.569251264	6.26
β_L (g$^-$, g$^+$)	-57.78	95.35	-143.45	173.58	176.99	-140.34	-179.24	-606.573103718	3.85
β_L (g$^-$, a)	-60.11	175.94	-63.83	173.75	176.83	-133.69	161.86	-606.577318852	1.20
β_L (g$^-$, g$^-$)	-73.30	-52.82	72.79	172.81	177.19	-135.49	160.85	-606.573076911	3.86
δ_L (g$^+$, g$^+$)	48.29	56.48	178.46	-172.39	175.76	-122.98	18.74	-606.572102338	4.48
δ_L (g$^+$, a)	82.48	-176.48	-53.92	-172.38	176.45	-114.30	12.49	-606.569970361	5.81
δ_L (g$^+$, g$^-$)	52.58	82.04	45.73	-172.85	175.89	-128.17	21.36	-606.567208154	7.55
δ_L (a, g$^+$)						Not found			
δ_L (a, a)						Not found			
δ_L (a, g$^-$)						Not found			
δ_L (g$^-$, g$^+$)	-71.02	80.00	-158.67	-173.49	176.34	-113.21	17.88	-606.570045945	5.77
δ_L (g$^-$, a)	-59.63	177.97	-60.11	-173.18	176.30	-125.29	24.89	-606.574745169	2.82
δ_L (g$^-$, g$^-$)	-68.04	-49.02	77.36	-174.63	176.23	-121.42	21.65	-606.570537874	5.46
γ_L (g$^+$, g$^+$)	38.84	55.63	177.60	-173.69	178.56	-84.04	57.00	-606.574092462	3.23
γ_L (g$^+$, a)	75.75	-176.37	-54.29	-173.93	-179.09	-85.85	65.77	-606.573420520	3.65
γ_L (g$^+$, g$^-$)	156.58	-86.84	42.32	-174.15	178.68	-85.88	57.07	-606.568735971	6.59
γ_L (a, g$^+$)	**-172.47**	**65.84**	**-172.66**	**-175.39**	**-178.22**	**-86.42**	**70.71**	**-606.579234518**	**0.00**
γ_L (a, a)	-153.59	-178.61	-56.29	-176.34	-177.31	-86.25	75.87	-606.577247581	1.25
γ_L (a, g$^-$)	-154.27	-53.89	71.10	-176.23	-177.42	-86.57	75.25	-606.576374442	1.79
γ_L (g$^-$, g$^+$)	-82.07	66.87	-171.07	-175.06	-178.86	-85.83	66.36	-606.575977316	2.04
γ_L (g$^-$, a)	-60.39	174.60	-63.76	-175.85	-178.52	-86.70	69.08	-606.578552462	0.43
γ_L (g$^-$, g$^-$)	-79.15	-62.44	63.44	-175.09	-178.68	-86.28	66.89	-606.570537874	5.46
ε_L (g$^+$, g$^+$)						Not found			
ε_L (g$^+$, a)						Not found			
ε_L (g$^+$, g$^-$)						Not found			

final geometry	χ_1 (7-8-13-14)	χ_2 (8-13-14-15)	χ_2' (8-13-14-17)	ω_0 (2-3-7-8)	ω_1 (8-9-26-27)	ϕ (3-7-8-9)	ψ (7-8-9-26)	energy (hartree)	$\Delta E_{rel.}$ (kcal.mol^{-1})
ε_L (a, g$^+$)						Not found			
ε_L (a, a)						Not found			
ε_L (a, g$^-$)						Not found			
ε_L (g$^-$, g$^+$)						Not found			
ε_L (g$^-$, a)						Not found			
ε_L (g$^-$, g$^-$)						Not found			
α_L (g$^+$, g$^+$)						Not found			
α_L (g$^+$, a)						Not found			
α_L (g$^+$, g$^-$)						Not found			
α_L (a, g$^+$)	-178.37	55.55	177.71	-173.41	-179.45	-82.89	-19.53	-606.571049303	5.14
α_L (a, a)	-158.67	161.22	-76.96	-173.89	-179.29	-66.55	-36.82	-606.566682414	7.88
α_L (a, g$^-$)	-173.90	-84.80	40.96	-173.54	-179.11	-71.89	-30.39	-606.567388067	7.43
α_L (g$^-$, g$^+$)						Not found			
α_L (g$^-$, a)						Not found			
α_L (g$^-$, g$^-$)						Not found			

[a] The global minimum corresponds to γ_L (*a, g*$^+$) conformation having a total energy of -606.579234518 hartree. This value is taken as reference value, corresponding to a relative energy 0.00 kcal mol^{-1}

Table S2: Torsional angles and total energy values for backbone and side-chain conformers of $CH_3CO–Leu–NHCH_3$ optimized at B3LYP/6-31G(d) level of theory. Calculated relative energies ($\Delta E_{rel.}$)[a] and numbering definition of the torsional angles which have been taken into account are also shown.

Final Geometry	χ_1 (7-8-13-14)	χ_2 (8-13-14-15)	χ_3 (8-13-14-17)	ω_0 (2-3-7-8)	ω_1 (8-9-26-27)	ϕ (3-7-8-9)	ψ (7-8-9-26)	Energy (Hartree)	$\Delta E_{rel.}$ (kcal.mol^{-1})
α_D (g^+, g^+)						Not found			
α_D (g^+, a)	62.32	139.96	-96.83	170.48	-173.65	48.35	42.49	-613.780530282	9.48
α_D (g^+, g^-)						Not found			
α_D (a, g^+)	-155.35	68.48	-168.36	166.56	-176.14	65.04	34.79	-613.784916243	6.72
α_D (a, a)						Not found			
α_D (a, g^-)						Not found			
α_D (g^-, g^+)	-82.54	63.81	-172.27	166.09	-177.08	69.59	25.47	-613.784206302	7.17
α_D (g^-, a)						Not found			
α_D (g^-, g^-)	-80.68	-65.91	61.78	165.79	-177.70	68.64	26.08	-613.782953365	7.96
ε_D (g^+, g^+)	56.44	72.29	-163.92	-162.92	-178.79	48.50	-152.32	-613.778120272	10.99
ε_D (g^+, a)	57.44	147.25	-90.17	-165.32	175.80	43.51	-134.15	-613.777746953	11.22
ε_D (g^+, g^-)	55.79	-66.67	63.16	-162.28	179.84	44.01	-146.34	-613.772822572	14.31
ε_D (a, g^+)	-160.81	58.58	-178.44	-158.09	-179.99	72.33	161.88	-613.778978410	10.45
ε_D (a, a)	-169.27	144.94	-92.10	-159.67	176.22	78.99	138.20	-613.776035197	12.30
ε_D (a, g^-)						Not found			
ε_D (g^-, g^+)						Not found			
ε_D (g^-, a)						Not found			
ε_D (g^-, g^-)						Not found			
γ_D (g^+, g^+)						Not found			
γ_D (g^+, a)	67.61	140.02	-97.08	173.82	-177.58	52.91	-31.92	-613.783257496	7.77
γ_D (g^+, g^-)	69.13	-75.41	53.98	168.50	-178.42	52.75	-13.19	-613.780578200	9.45
γ_D (a, g^+)	-177.98	56.84	-178.95	174.30	-179.88	72.92	-58.17	-613.792000220	2.28
γ_D (a, a)	-156.51	168.05	-68.02	175.47	177.23	75.02	-65.96	-613.789585125	3.79
γ_D (a, g^-)	-170.51	-77.62	50.16	175.28	-179.00	73.47	-56.00	-613.788890088	4.23
γ_D (g^-, g^+)	-75.86	68.39	-167.93	174.80	-177.96	73.84	-56.37	-613.789237183	4.01
γ_D (g^-, a)	-59.71	173.27	-63.04	175.67	-178.88	73.37	-56.04	-613.791412818	2.65
γ_D (g^-, g^-)	-70.02	-58.05	70.15	-173.86	-178.78	73.83	-56.80	-613.788015107	4.78
δ_D (g^+, g^+)	58.09	91.89	-144.63	167.09	-173.89	-171.31	-28.52	-613.780567343	9.45
δ_D (g^+, a)	66.17	165.47	-71.64	168.46	-173.43	-170.15	-29.89	-613.780830859	9.29
δ_D (g^+, g^-)						Not found			
δ_D (a, g^+)						Not found			

Final Geometry	χ_1 (7-8-13-14)	χ_2 (8-13-14-15)	χ_3 (8-13-14-17)	ω_0 (2-3-7-8)	ω_1 (8-9-26-27)	ϕ (3-7-8-9)	ψ (7-8-9-26)	Energy (Hartree)	$\Delta E_{rel.}$ (kcal.mol^{-1})
δ_D (a, a)						Not found			
δ_D (a, g$^-$)						Not found			
δ_D (g$^-$, g$^+$)						Not found			
δ_D (g$^-$, a)						Not found			
δ_D (g$^-$, g$^-$)						Not found			
β_L (g$^+$, g$^+$)	53.04	69.78	-166.20	173.54	178.57	-153.62	168.47	-613.791819189	2.39
β_L (g$^+$, a)	76.09	176.04	-59.96	173.97	165.97	-154.95	165.97	-613.790740464	3.07
β_L (g$^+$, g$^-$)	69.64	-55.58	72.95	175.36	175.75	-152.53	160.11	-613.788058965	4.75
β_L (a, g$^+$)	-174.46	63.46	-173.39	179.39	178.42	-153.32	145.09	-613.792077168	2.23
β_L (a, a)	-177.36	146.29	-90.19	-178.06	178.39	-153.06	137.63	-613.789688655	3.73
β_L (a, g$^-$)						Not found			
β_L (g$^-$, g$^+$)	-59.58	91.38	-143.43	169.87	177.56	-130.21	155.04	-613.790223230	3.39
β_L (g$^-$, a)	-62.60	172.25	-63.69	170.83	177.40	-130.33	154.94	-613.793744758	1.18
β_L (g$^-$, g$^-$)	-73.61	-56.51	71.01	171.47	177.07	-128.72	153.00	-613.790234450	3.39
δ_L (g$^+$, g$^+$)	49.78	57.79	-178.28	-167.71	174.18	-124.99	16.42	-613.788853004	4.25
δ_L (g$^+$, a)	79.02	179.52	-56.28	-169.44	174.13	-116.23	11.30	-613.788159035	4.69
δ_L (g$^+$, g$^-$)	55.25	-80.15	49.15	-168.87	172.31	-125.81	15.86	-613.784841833	6.77
δ_L (a, g$^+$)						Not found			
δ_L (a, a)						Not found			
δ_L (a, g$^-$)						Not found			
δ_L (g$^-$, g$^+$)	-87.93	59.39	-175.96	-170.54	174.01	-114.61	18.56	-613.788808664	4.28
δ_L (g$^-$, a)	-62.15	175.32	-60.84	-169.84	174.49	-122.27	17.36	-613.791160171	2.81
δ_L (g$^-$, g$^-$)	-84.56	-65.09	61.99	-171.38	174.12	-117.39	17.99	-613.787761992	4.94
γ_L (g$^+$, g$^+$)	41.46	55.39	179.57	-174.32	175.69	-81.71	52.16	-613.790963752	2.93
γ_L (g$^+$, a)	73.87	-177.46	-53.54	-174.65	-176.29	-84.31	70.56	-613.791094703	2.85
γ_L (g$^+$, g$^-$)	44.37	-86.46	43.89	-174.83	176.52	-82.26	53.65	-613.786475791	5.75
γ_L (a, g$^+$)	**-170.01**	**65.26**	**-171.25**	**-177.69**	**-174.94**	**-82.83**	**75.22**	**-613.795632706**	**0.00**
γ_L (a, a)	-151.17	177.55	-58.13	-177.49	-173.42	-82.64	79.20	-613.794122523	0.95
γ_L (a, g$^-$)	-150.99	-57.53	69.38	-177.14	-173.95	-83.16	78.33	-613.792928646	1.70
γ_L (g$^-$, g$^+$)	-82.59	64.67	-171.11	-176.29	-176.55	-83.28	68.99	-613.793108073	1.58
γ_L (g$^-$, a)	-60.24	174.29	-61.98	-178.65	-175.39	-83.53	73.71	-613.795113522	0.33
γ_L (g$^-$, g$^-$)	-71.99	-57.26	70.60	-175.39	-176.52	-83.91	69.52	-613.791878623	2.36
ε_L (g$^+$, g$^+$)						Not found			
ε_L (g$^+$, a)						Not found			
ε_L (g$^+$, g$^-$)						Not found			

Final Geometry	χ_1 (7-8-13-14)	χ_2 (8-13-14-15)	χ_3 (8-13-14-17)	ω_0 (2-3-7-8)	ω_1 (8-9-26-27)	ϕ (3-7-8-9)	ψ (7-8-9-26)	Energy (Hartree)	$\Delta E_{rel.}$ (kcal.mol^{-1})
ε_L (a, g$^+$)						Not found			
ε_L (a, a)						Not found			
ε_L (a, g$^-$)						Not found			
ε_L (g$^-$, g$^+$)						Not found			
ε_L (g$^-$, a)						Not found			
ε_L (g$^-$, g$^-$)						Not found			
α_L (g$^+$, g$^+$)						Not found			
α_L (g$^+$, a)						Not found			
α_L (g$^+$, g$^-$)						Not found			
α_L (a, g$^+$)						Not found			
α_L (a, a)						Not found			
α_L (a, g$^-$)	-173.00	-83.19	45.08	-168.52	176.50	-77.45	-28.26	-613.784506269	6.98
α_L (g$^-$, g$^+$)						Not found			
α_L (g$^-$, a)						Not found			
α_L (g$^-$, g$^-$)						Not found			

[a] The global minimum corresponds to γ_L (*a, g*$^+$) conformation having a total energy of -613.795632706 hartree. This value is taken as reference value, corresponding to a relative energy 0.00 kcal mol^{-1}

Table S3: Total energy values and calculated relative energies for all the conformations of $CH_3CO–Leu–NHCH_3$ obtained at IPCM/B3LYP/6-31G(d) level of theory in three different solvents.

conformations	IPCM/B3LYP/6-31G(d) *clhoroform* (ε=4.90)		IPCM/B3LYP/6-31G(d) *acetonitrile* (ε=36.64)		IPCM/B3LYP/6-31G(d) *water* (ε=78.39)	
	energy (Hartree)	$\Delta E_{rel.}$ (kcal.mol^{-1})	energy (Hartree)	$\Delta E_{rel.}$ (kcal.mol^{-1})	energy (Hartree)	$\Delta E_{rel.}$ (kcal.mol^{-1})
α_D (g^+, a)	-613.7957873	8.33	-613.8033879	8.40	-613.8041868	8.51
α_D (a, g^+)	-613.8011969	4.94	-613.8091335	4.79	-613.8099635	4.88
α_D (g^-, g^+)	-613.8006054	5.31	-613.8077061	5.69	-613.8084181	5.85
α_D (g^-, g^-)	-613.8019843	4.45	-613.8111625	3.52	-613.8121232	3.53
ε_D (g^+, g^+)	-613.7913671	11.11	-613.7972831	12.23	-613.7978815	12.46
ε_D (g^+, a)	-613.7923821	10.47	-613.7988721	11.23	-613.7995261	11.43
ε_D (g^+, g^-)	-613.7860868	14.42	-613.7921431	15.46	-613.7927682	15.67
ε_D (a, g^+)	-613.7952828	8.65	-613.8027514	8.80	-613.8035183	8.93
ε_D (a, a)	-613.7916595	10.92	-613.7986831	11.35	-613.7993941	11.51
γ_D (g^+, a)	-613.7977326	7.11	-613.8034299	8.37	-613.8039794	8.64
γ_D (g^+, g^-)	-613.7947814	8.97	-613.8009526	9.93	-613.8015681	10.15
γ_D (a, g^+)	**-613.8090686**	**0.00**[a]	**-613.8167734**	**0.00**[b]	**-613.8177439**	**0.00**[c]
γ_D (a, a)	-613.8050937	2.49	-613.8119282	3.04	-613.8126214	3.21
γ_D (a, g^-)	-613.8023901	4.19	-613.8080717	5.46	-613.8086304	5.72
γ_D (g^-, g^+)	-613.8043820	2.94	-613.8107878	3.76	-613.8114169	3.97
γ_D (g^-, a)	-613.8056677	2.13	-613.8113538	3.40	-613.8119089	3.66
γ_D (g^-, g^-)	-613.8042805	3.00	-613.8112077	3.49	-613.8118873	3.68
δ_D (g^+, g^+)	-613.7981059	6.88	-613.8067859	6.27	-613.8077236	6.29
δ_D (g^+, a)	-613.7961629	8.10	-613.8030119	8.64	-613.8037126	8.80
β_L (g^+, g^+)	-613.8031934	3.69	-613.8073540	5.91	-613.8077444	6.27
β_L (g^+, a)	-613.8034982	3.50	-613.8082851	5.33	-613.8087366	5.65
β_L (g^+, g^-)	-613.8004952	5.38	-613.8052389	7.24	-613.805688	7.57
β_L (a, g^+)	-613.8063344	1.72	-613.8159238	0.53	-613.8166116	0.71
β_L (a, a)	-613.8041666	3.08	-613.8097950	4.38	-613.8103299	4.65
β_L (g^-, g^+)	-613.8040891	3.12	-613.8093220	4.68	-613.8098150	4.98
β_L (g^-, a)	-613.8072411	1.15	-613.8128920	2.44	-613.8134470	2.70
β_L (g^-, g^-)	-613.8037954	3.31	-613.8093533	4.66	-613.8098956	4.92
δ_L (g^+, g^+)	-613.8023188	4.24	-613.8079673	5.53	-613.8085232	5.79
δ_L (g^+, a)	-613.8038270	3.29	-613.8104092	3.99	-613.8110597	4.19
δ_L (g^+, g^-)	-613.7988830	6.39	-613.8048280	7.50	-613.8054155	7.74
δ_L (g^-, g^+)	-613.8058213	2.04	-613.8133965	2.12	-613.8141619	2.25
δ_L (g^-, a)	-613.8073729	1.06	-613.8151815	1.00	-613.8160756	1.05

conformations	IPCM/B3LYP/6-31G(d) *clhoroform* (ε=4.90)		IPCM/B3LYP/6-31G(d) *acetonitrile* (ε=36.64)		IPCM/B3LYP/6-31G(d) *water* (ε=78.39)	
	energy (Hartree)	$\Delta E_{rel.}$ (kcal.mol^{-1})	energy (Hartree)	$\Delta E_{rel.}$ (kcal.mol^{-1})	energy (Hartree)	$\Delta E_{rel.}$ (kcal.mol^{-1})
δ_L (g^-, g^-)	-613.8022169	4.30	-613.8083031	5.32	-613.8089052	5.55
γ_L (g^+, g^+)	-613.8056171	2.17	-613.8120317	2.98	-613.8126759	3.18
γ_L (g^+, a)	-613.8055335	2.22	-613.8112854	3.44	-613.8118447	3.70
γ_L (g^+, g^-)	-613.7978932	7.01	-613.8029786	8.66	-613.8034951	8.94
γ_L (a, g^+)	-613.8087002	0.23	-613.8142340	1.59	-613.8147523	1.88
γ_L (a, a)	-613.8067584	1.45	-613.8122389	2.85	-613.8128021	3.10
γ_L (a, g^-)	-613.8066677	1.51	-613.8122267	2.85	-613.8127618	3.13
γ_L (g^-, g^+)	-613.8062318	1.78	-613.8112913	3.44	-613.8117735	3.75
γ_L (g^-, a)	-613.8088306	0.15	-613.8143747	1.51	-613.8149064	1.78
γ_L (g^-, g^-)	-613.8060854	1.87	-613.8121158	2.92	-613.8127114	3.16
α_L (a, g^-)	-613.8012337	4.92	-613.8091282	4.80	-613.8099376	4.90

[a] The global minimum corresponds to γ_D (*a, g*$^+$) conformation having a total energy of -613.8090686 hartree in chloroform. This value is taken as reference value, corresponding to a relative energy 0.00 kcal mol^{-1}

[b] The global minimum corresponds to γ_D (*a, g*$^+$) conformation having a total energy of -613.8167734 hartree in acetonitrile. This value is taken as reference value, corresponding to a relative energy 0.00 kcal mol^{-1}

[c] The global minimum corresponds to γ_D (*a, g*$^+$) conformation having a total energy of -613.8177439 hartree in water. This value is taken as reference value, corresponding to a relative energy 0.00 kcal mol^{-1}

Table S4: Torsional angles and total energy values for backbone and side-chain conformers of $CH_3CO–Leu–NHCH_3$ optimized at PB-SCRF/B3LYP/6-31G(d) level of theory using chloroform (ε= 4.90) as solvent. Calculated relative energies ($\Delta E_{rel.}$)[a] and numbering definition of the torsional angles which have been taken into account are also shown.

Final Geometry	χ_1 (7-8-13-14)	χ_2 (8-13-14-15)	χ_3 (8-13-14-17)	ω_0 (2-3-7-8)	ω_1 (8-9-26-27)	ϕ (3-7-8-9)	ψ (7-8-9-26)	Energy (Hartree)	$\Delta E_{rel.}$ (kcal.mol^{-1})
α_D (g^+, g^+)						Not found			
α_D (g^+, a)	63.70	142.83	-94.24	173.36	-176.78	48.56	42.79	-613.797251	8.17
α_D (g^+, g^-)						Not found			
α_D (a, g^+)	-154.80	68.48	-168.44	168.38	-178.58	63.60	36.51	-613.801710	5.37
α_D (a, g^+)$_2$	-169.49	65.26	-171.32	-173.33	179.83	82.01	114.76	-613.797730	7.87
α_D (a, a)	-122.38	171.31	-64.95	170.91	-179.28	67.57	30.99	-613.800028	6.43
α_D (a, g^-)						Not found			
α_D (g^-, g^+)	-75.44	70.98	-165.69	170.08	-179.63	68.91	25.25	-613.801613	5.43
α_D (g^-, a)						Not found			
α_D (g^-, g^-)	-69.28	-57.65	70.93	170.64	-179.89	69.49	23.72	-613.800192	6.33
ε_D (g^+, g^+)	56.52	71.88	-164.36	-170.66	-176.55	49.29	-154.65	-613.794961	9.61
ε_D (g^+, a)	60.85	148.55	-89.06	-170.20	-178.36	45.27	-140.50	-613.793791	10.34
ε_D (g^+, g^-)	59.05	-68.86	60.84	-167.96	-176.12	45.17	-152.68	-613.789347	13.13
ε_D (a, g^+)						Not found			
ε_D (a, a)						Not found			
ε_D (a, g^-)						Not found			
ε_D (g^-, g^+)						Not found			
ε_D (g^-, a)						Not found			
ε_D (g^-, g^-)						Not found			
γ_D (g^+, g^+)						Not found			
γ_D (g^+, a)	72.64	141.94	-95.38	177.96	-177.22	58.40	-35.32	-613.798670	7.28
γ_D (g^+, g^-)	72.37	-75.39	54.07	173.85	-178.84	52.25	-16.11	-613.796399	8.71
γ_D (a, g^+)	-176.16	59.86	-176.15	173.69	-179.73	72.82	-57.20	-613.806972	2.07
γ_D (a, a)	-150.28	171.57	-64.55	175.95	176.98	75.28	-67.64	-613.804779	3.45
γ_D (a, g^-)	-166.39	-75.55	52.33	174.54	-179.51	74.48	-57.99	-613.803688	4.13
γ_D (g^-, g^+)	-71.80	73.69	-162.93	175.28	-178.77	73.44	-56.06	-613.804764	3.46
γ_D (g^-, a)	-55.45	178.47	-57.90	175.69	-179.02	73.88	-55.85	-613.807153	1.96
γ_D (g^-, g^-)	-66.05	-54.25	74.09	174.90	179.23	73.97	-56.01	-613.803343	4.35
δ_D (g^+, g^+)	61.68	91.12	-145.61	166.88	-175.32	-171.56	-25.85	-613.796833	8.43
δ_D (g^+, a)	66.92	164.41	-72.75	168.35	-176.02	-170.72	-26.21	-613.797718	7.88
δ_D (g^+, g^-)						Not found			

Final Geometry	χ_1 (7-8-13-14)	χ_2 (8-13-14-15)	χ_3 (8-13-14-17)	ω_0 (2-3-7-8)	ω_1 (8-9-26-27)	ϕ (3-7-8-9)	ψ (7-8-9-26)	Energy (Hartree)	$\Delta E_{rel.}$ (kcal.mol^{-1})
δ_D (a, g$^+$)						Not found			
δ_D (a, a)						Not found			
δ_D (a, g$^-$)						Not found			
δ_D (g$^-$, g$^+$)						Not found			
δ_D (g$^-$, a)						Not found			
δ_D (g$^-$, g$^-$)						Not found			
β_L (g$^+$, g$^+$)	50.47	68.14	-167.94	175.24	178.80	-152.50	165.84	-613.808300	1.24
β_L (g$^+$, a)	72.39	172.23	-64.16	175.00	177.21	-154.06	159.85	-613.807271	1.88
β_L (g$^+$, g$^-$)	58.89	-67.79	61.29	175.99	179.95	-154.13	163.34	-613.804142	3.85
β_L (a, g$^+$)	179.66	61.60	-174.99	-179.02	179.02	-147.03	133.00	-613.809227	0.66
β_L (a, a)	179.11	146.47	-90.25	-178.49	178.94	-149.96	132.92	-613.806943	2.09
β_L (a, g$^-$)						Not found			
β_L (g$^-$, g$^+$)	-65.96	84.38	-152.64	173.08	177.36	-130.14	144.12	-613.806805	2.18
β_L (g$^-$, a)	-62.18	170.68	-65.41	173.49	176.92	-129.92	145.57	-613.810039	0.15
β_L (g$^-$, g$^-$)	-75.17	-59.40	68.23	172.82	177.28	-127.24	140.96	-613.806146	2.59
δ_L (g$^+$, g$^+$)	48.56	59.82	-176.26	-172.93	173.26	-127.54	17.01	-613.805476	3.01
δ_L (g$^+$, a)	79.95	-178.93	-54.78	-170.71	175.26	-117.48	9.03	-613.803859	4.02
δ_L (g$^+$, g$^-$)	51.00	-81.50	47.55	-173.69	172.95	-131.95	22.49	-613.801181	5.70
δ_L (a, g$^+$)						Not found			
δ_L (a, a)						Not found			
δ_L (a, g$^-$)						Not found			
δ_L (g$^-$, g$^+$)	-90.14	59.54	-176.04	-174.32	174.99	-111.75	17.42	-613.806629	2.29
δ_L (g$^-$, a)	-64.04	173.02	-63.34	-172.43	175.32	-123.81	15.27	-613.808228	1.28
δ_L (g$^-$, g$^-$)	-89.63	-68.68	58.28	-173.81	175.16	-114.50	15.48	-613.804592	3.56
γ_L (g$^+$, g$^+$)	41.01	57.03	-178.73	-173.33	175.32	-83.34	52.65	-613.803916	3.99
γ_L (g$^+$, a)	72.29	-178.47	-54.74	-175.37	-176.75	-85.27	74.71	-613.802937	4.60
γ_L (g$^+$, g$^-$)	41.98	-85.32	44.92	-174.46	175.75	-84.99	56.16	-613.798643	7.30
γ_L (a, g$^+$)	**-173.12**	**60.53**	**-176.07**	**-177.34**	**-174.73**	**-83.36**	**77.86**	**-613.810272**	**0.00**
γ_L (a, a)	-153.20	175.59	-60.23	-176.69	-172.20	-85.18	79.25	-613.808341	1.21
γ_L (a, g$^-$)	-153.24	-58.84	68.15	177.59	-173.11	-83.61	80.42	-613.806877	2.13
γ_L (g$^-$, g$^+$)	-89.41	58.80	-176.76	-176.51	-176.33	-85.07	71.51	-613.807766	1.57
γ_L (g$^-$, a)	-63.63	170.48	-65.90	-178.03	-175.39	-84.61	75.69	-613.809877	0.25
γ_L (g$^-$, g$^-$)	-86.88	-69.72	57.39	-176.48	-176.18	-84.82	70.30	-613.806138	2.59
ε_L (g$^+$, g$^+$)						Not found			
ε_L (g$^+$, a)						Not found			

Final Geometry	χ_1 (7-8-13-14)	χ_2 (8-13-14-15)	χ_3 (8-13-14-17)	ω_0 (2-3-7-8)	ω_1 (8-9-26-27)	ϕ (3-7-8-9)	ψ (7-8-9-26)	Energy (Hartree)	$\Delta E_{rel.}$ (kcal.mol^{-1})
ε_L (g^+, g^-)						Not found			
ε_L (a, g^+)						Not found			
ε_L (a, a)						Not found			
ε_L (a, g^-)						Not found			
ε_L (g^-, g^+)						Not found			
ε_L (g^-, a)						Not found			
ε_L (g^-, g^-)						Not found			
α_L (g^+, g^+)						Not found			
α_L (g^+, a)						Not found			
α_L (g^+, g^-)						Not found			
α_L (a, g^+)						Not found			
α_L (a, a)						Not found			
α_L (a, g^-)	-172.43	-81.15	47.06	-169.82	177.66	-74.66	-33.46	-613.802267	5.02
α_L (g^-, g^+)						Not found			
α_L (g^-, a)						Not found			
α_L (g^-, g^-)						Not found			

[a] The global minimum corresponds to γ_L (*a*, g^+) conformation having a total energy of -613.810272 hartree. This value is taken as reference value, corresponding to a relative energy 0.00 kcal mol^{-1}

Table S5: Torsional angles and total energy values for backbone and side-chain conformers of $CH_3CO–Leu–NHCH_3$ optimized at PB-SCRF/B3LYP/6-31G(d) level of theory using acetonitrile (ε= 36.64) as solvent. Calculated relative energies ($\Delta E_{rel.}$)[a] and numbering definition of the torsional angles which have been taken into account are also shown.

Final Geometry	χ_1 (7-8-13-14)	χ_2 (8-13-14-15)	χ_2' (8-13-14-17)	ω_0 (2-3-7-8)	ω_1 (8-9-26-27)	ϕ (3-7-8-9)	ψ (7-8-9-26)	Energy (Hartree)	$\Delta E_{rel.}$ (kcal.mol^{-1})
α_D (g^+, g^+)						Not found			
α_D (g^+, a)	63.62	144.96	-92.38	-175.71	-178.23	47.51	44.38	-613.804738	7.08
α_D (g^+, g^-)						Not found			
α_D (a, g^+)	-153.28	69.51	-167.41	171.02	179.61	63.01	37.69	-613.809449	4.12
α_D (a, g^+)$_2$	-170.52	63.67	-172.38	-178.60	-176.22	73.32	90.68	-613.805503	6.60
α_D (a, a)						Not found			
α_D (a, g^-)						Not found			
α_D (g^-, g^+)	-72.86	73.48	-163.36	173.86	178.19	66.66	26.48	-613.809698	3.97
α_D (g^-, a)	-117.00	170.28	-66.12	174.01	177.03	67.72	29.51	-613.807879	5.11
α_D (g^-, g^-)	-65.92	-54.01	74.64	174.26	177.82	66.05	27.95	-613.807851	5.13
ε_D (g^+, g^+)	61.89	68.50	-167.75	-174.03	-175.71	54.20	-167.23	-613.803038	8.15
ε_D (g^+, a)	85.83	145.12	-92.23	-175.41	-173.36	47.91	-149.07	-613.801702	8.99
ε_D (g^+, g^-)	62.18	-71.32	58.47	-170.99	-174.73	47.61	-156.01	-613.797065	11.90
ε_D (a, g^+)						Not found			
ε_D (a, a)						Not found			
ε_D (a, g^-)						Not found			
ε_D (g^-, g^+)						Not found			
ε_D (g^-, a)						Not found			
ε_D (g^-, g^-)						Not found			
γ_D (g^+, g^+)						Not found			
γ_D (g^+, a)	74.31	140.48	-96.72	175.12	-177.55	58.26	-30.68	-613.804749	7.07
γ_D (g^+, g^-)	72.83	-75.59	53.93	173.88	-179.37	52.90	-15.22	-613.802600	8.42
γ_D (a, g^+)	-174.26	61.71	-174.37	175.03	179.91	72.84	-58.38	-613.812709	2.08
γ_D (a, a)	-148.62	172.91	-63.28	176.69	176.50	76.12	-68.10	-613.810956	3.18
γ_D (a, g^-)	-163.64	-73.08	54.86	175.23	179.45	74.25	-60.17	-613.810027	3.76
γ_D (g^-, g^+)	-69.98	75.29	-161.42	176.01	-178.46	73.14	-56.83	-613.810762	3.30
γ_D (g^-, a)	-54.47	178.36	-58.04	176.13	-178.94	74.16	-56.16	-613.812879	1.97
γ_D (g^-, g^-)	-64.34	-51.92	76.44	177.10	-179.99	73.04	-58.06	-613.809362	4.18
δ_D (g^+, g^+)	65.83	90.30	-146.69	168.98	-178.33	-163.15	-27.61	-613.804260	7.38
δ_D (g^+, a)	66.41	163.49	-73.65	169.22	-178.66	-168.91	-28.50	-613.804991	6.92
δ_D (g^+, g^-)						Not found			

Final Geometry	χ_1 (7-8-13-14)	χ_2 (8-13-14-15)	χ_2' (8-13-14-17)	ω_0 (2-3-7-8)	ω_1 (8-9-26-27)	ϕ (3-7-8-9)	ψ (7-8-9-26)	Energy (Hartree)	$\Delta E_{rel.}$ (kcal.mol^{-1})
δ_D (a, g$^+$)						Not found			
δ_D (a, a)						Not found			
δ_D (a, g$^-$)						Not found			
δ_D (g$^-$, g$^+$)						Not found			
δ_D (g$^-$, a)						Not found			
δ_D (g$^-$, g$^-$)						Not found			
β_L (g$^+$, g$^+$)	49.59	67.43	-168.72	177.55	179.67	-154.39	164.99	-613.814394	1.02
β_L (g$^+$, a)	59.29	148.31	-88.53	177.76	178.17	-151.57	156.92	-613.813174	1.79
β_L (g$^+$, g$^-$)	55.33	-70.95	58.15	177.31	-179.21	-155.09	163.14	-613.810399	3.53
β_L (a, g$^+$)	177.04	62.08	-174.41	-178.67	179.43	-142.75	130.21	-613.815557	0.29
β_L (a, a)	177.99	146.59	-90.27	-178.40	179.31	-144.64	131.11	-613.813362	1.67
β_L (a, g$^-$)						Not found			
β_L (g$^-$, g$^+$)						Not found			
β_L (g$^-$, a)	**-64.89**	**169.20**	**-67.01**	**176.57**	**176.93**	**-133.57**	**141.27**	**-613.816021**	**0.00**
β_L (g$^-$, g$^-$)						Not found			
δ_L (g$^+$, g$^+$)	47.66	59.74	-176.23	-174.45	173.77	-126.73	17.86	-613.812744	2.06
δ_L (g$^+$, a)	76.08	179.29	-57.02	-174.46	174.64	-130.76	18.85	-613.811189	3.03
δ_L (g$^+$, g$^-$)	49.74	-80.82	48.38	-173.66	172.64	-131.30	21.28	-613.807834	5.14
δ_L (a, g$^+$)						Not found			
δ_L (a, a)						Not found			
δ_L (a, g$^-$)						Not found			
δ_L (g$^-$, g$^+$)	-91.72	48.59	-177.06	-176.46	175.96	-110.52	12.69	-613.813547	1.55
δ_L (g$^-$, a)	-66.48	170.90	-65.55	-175.84	175.50	-122.86	17.49	-613.815502	0.33
δ_L (g$^-$, g$^-$)	-89.36	-70.31	56.63	-176.99	176.51	-109.35	10.84	-613.811821	2.64
γ_L (g$^+$, g$^+$)	38.91	58.20	-177.69	-174.02	175.20	-86.13	56.61	-613.808922	4.45
γ_L (g$^+$, a)	71.71	-178.50	-54.83	-176.02	-176.42	-85.50	75.20	-613.807590	5.29
γ_L (g$^+$, g$^-$)	39.94	-83.72	46.56	-175.37	175.67	-87.40	58.11	-613.803631	7.77
γ_L (a, g$^+$)	-174.63	58.27	-178.26	-177.82	-175.02	-84.89	80.36	-613.815815	0.13
γ_L (a, a)	-175.78	178.48	-61.36	-178.10	-172.60	-84.38	84.34	-613.814115	1.20
γ_L (a, g$^-$)	-155.01	-59.62	67.61	-177.73	-173.01	-84.15	81.32	-613.812172	2.42
γ_L (g$^-$, g$^+$)	-92.10	58.79	-176.85	-177.30	-176.05	-85.85	72.82	-613.813447	1.62
γ_L (g$^-$, a)	-69.03	164.38	-72.14	-178.12	-175.68	-84.87	76.26	-613.815479	0.34
γ_L (g$^-$, g$^-$)	-92.87	-71.07	55.88	-177.07	-176.59	-85.53	72.98	-613.811632	2.75
ε_L (g$^+$, g$^+$)						Not found			
ε_L (g$^+$, a)						Not found			

Final Geometry	χ_1 (7-8-13-14)	χ_2 (8-13-14-15)	χ_2' (8-13-14-17)	ω_0 (2-3-7-8)	ω_1 (8-9-26-27)	ϕ (3-7-8-9)	ψ (7-8-9-26)	Energy (Hartree)	$\Delta E_{rel.}$ (kcal.mol^{-1})
ε_L (g^+, g^-)						Not found			
ε_L (a, g^+)						Not found			
ε_L (a, a)						Not found			
ε_L (a, g^-)						Not found			
ε_L (g^-, g^+)	-90.08	58.13	-177.52	174.64	176.30	-117.68	141.68	-613.813683	1.47
ε_L (g^-, a)						Not found			
ε_L (g^-, g^-)	-88.50	-71.45	55.54	175.37	177.71	-114.74	133.16	-613.810778	3.29
α_L (g^+, g^+)						Not found			
α_L (g^+, a)						Not found			
α_L (g^+, g^-)						Not found			
α_L (a, g^+)						Not found			
α_L (a, a)						Not found			
α_L (a, g^-)	-170.85	-81.07	47.23	-172.69	179.30	-71.49	-35.52	-613.810564	3.42
α_L (g^-, g^+)						Not found			
α_L (g^-, a)						Not found			
α_L (g^-, g^-)						Not found			

[a] The global minimum corresponds to β_L (*g*$^-$, *a*) conformation having a total energy of -613.816021 hartree. This value is taken as reference value, corresponding to a relative energy 0.00 kcal mol^{-1}

Table S6: Torsional angles and total energy values for backbone and side-chain conformers of $CH_3CO–Leu–NHCH_3$ optimized at PB-SCRF/B3LYP/6-31G(d) level of theory using water (ε= 78.39) as solvent. Calculated relative energies ($\Delta E_{rel.}$)[a] and numbering definition of the torsional angles which have been taken into account are also shown.

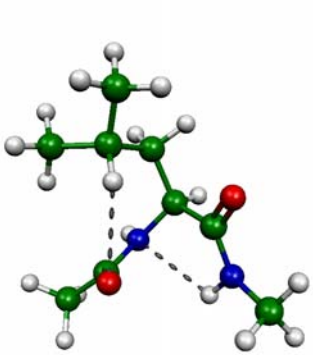
Final Geometry	χ_1 (7-8-13-14)	χ_2 (8-13-14-15)	χ_2' (8-13-14-17)	ω_0 (2-3-7-8)	ω_1 (8-9-26-27)	ϕ (3-7-8-9)	ψ (7-8-9-26)	Energy (Hartree)	$\Delta E_{rel.}$ (kcal.mol^{-1})
α_D (g^+, g^+)						Not found			
α_D (g^+, a)	65.11	146.12	-91.26	177.45	-179.61	47.67	43.43	-613.806327	7.23
α_D (g^+, g^-)						Not found			
α_D (a, g^+)	-153.45	70.03	-166.83	174.23	179.41	61.46	39.34	-613.812377	3.44
α_D (a, g^+)$_2$	-152.24	70.36	-166.47	173.19	179.78	62.59	37.33	-613.812009	3.67
α_D (a, a)	-119.86	171.36	-65.04	175.01	178.90	65.89	30.90	-613.810541	4.59
α_D (a, g^-)						Not found			
α_D (g^-, g^+)	-71.30	73.39	-163.49	175.13	178.83	65.73	27.03	-613.811727	3.84
α_D (g^-, a)						Not found			
α_D (g^-, g^-)	-66.24	-54.52	74.12	176.38	179.52	65.11	28.41	-613.809956	4.96
ε_D (g^+, g^+)	60.93	69.10	-167.34	-175.48	-175.71	53.84	-165.60	-613.805864	7.52
ε_D (g^+, a)	67.05	145.40	-91.95	-175.24	-172.88	48.46	-150.30	-613.802928	9.37
ε_D (g^+, g^-)	63.57	-72.30	57.63	-174.10	-172.51	49.35	-161.83	-613.800212	11.07
ε_D (a, g^+)						Not found			
ε_D (a, a)						Not found			
ε_D (a, g^-)						Not found			
ε_D (g^-, g^+)						Not found			
ε_D (g^-, a)						Not found			
ε_D (g^-, g^-)						Not found			
γ_D (g^+, g^+)						Not found			
γ_D (g^+, a)	75.99	140.83	-96.41	175.47	-178.61	59.01	-30.82	-613.806660	7.02
γ_D (g^+, g^-)	74.05	-73.99	55.58	174.88	179.63	51.58	-15.46	-613.804259	8.53
γ_D (a, g^+)	-172.95	63.01	-173.16	174.81	-179.95	72.87	-57.89	-613.814282	2.24
γ_D (a, a)	-147.65	173.60	-62.63	177.33	177.25	75.30	-68.46	-613.812426	3.41
γ_D (a, g^-)	-146.60	-61.10	66.44	176.74	177.48	75.62	-66.98	-613.810329	4.72
γ_D (g^-, g^+)	-66.54	80.07	-156.74	178.38	-178.06	72.28	-56.69	-613.812174	3.56
γ_D (g^-, a)	-53.29	179.56	-56.79	175.91	-178.63	73.86	-55.40	-613.814644	2.01
γ_D (g^-, g^-)	-63.83	-52.15	76.19	175.51	-178.88	73.78	-56.73	-613.810831	4.41
δ_D (g^+, g^+)	66.02	90.44	-146.56	170.31	-179.99	-162.98	-28.01	-613.806518	7.11
δ_D (g^+, a)	68.95	164.58	-75.48	169.92	-179.86	-164.96	-29.36	-613.807497	6.50
δ_D (g^+, g^-)						Not found			

Final Geometry	χ_1 (7-8-13-14)	χ_2 (8-13-14-15)	χ_2' (8-13-14-17)	ω_0 (2-3-7-8)	ω_1 (8-9-26-27)	ϕ (3-7-8-9)	ψ (7-8-9-26)	Energy (Hartree)	$\Delta E_{rel.}$ (kcal.mol^{-1})
δ_D (a, g$^+$)						Not found			
δ_D (a, a)						Not found			
δ_D (a, g$^-$)						Not found			
δ_D (g$^-$, g$^+$)						Not found			
δ_D (g$^-$, a)						Not found			
δ_D (g$^-$, g$^-$)						Not found			
β_L (g$^+$, g$^+$)	47.18	61.46	-175.68	169.74	-169.72	-155.23	167.60	-613.815846	1.26
β_L (g$^+$, a)	56.46	146.97	-89.91	177.23	177.48	-149.22	154.14	-613.814683	1.99
β_L (g$^+$, g$^-$)	53.69	-72.71	56.45	177.08	179.10	-154.45	163.15	-613.811756	3.83
β_L (a, g$^+$)	175.30	60.53	-175.78	-178.43	179.99	-135.92	124.42	-613.817725	0.08
β_L (a, a)	178.22	144.75	-92.03	-178.01	179.29	-145.94	130.79	-613.815366	1.56
β_L (a, g$^-$)						Not found			
β_L (g$^-$, g$^+$)						Not found			
β_L (g$^-$, a)	**-65.52**	**168.32**	**-67.89**	**176.39**	**177.34**	**-131.92**	**138.40**	**-613.817853**	**0.00**
β_L (g$^-$, g$^-$)						Not found			
δ_L (g$^+$, g$^+$)	47.99	59.42	-176.55	-175.47	173.97	-125.50	17.05	-613.814854	1.88
δ_L (g$^+$, a)	76.95	178.38	-57.83	-176.52	175.62	-122.09	13.95	-613.813380	2.81
δ_L (g$^+$, g$^-$)	50.28	-80.59	48.34	-174.79	173.24	-132.16	23.25	-613.810055	4.89
δ_L (a, g$^+$)						Not found			
δ_L (a, a)						Not found			
δ_L (a, g$^-$)						Not found			
δ_L (g$^-$, g$^+$)	-92.19	59.92	-175.64	-177.87	174.92	-110.55	15.29	-613.815668	1.37
δ_L (g$^-$, a)	-66.30	170.63	-65.83	-176.05	175.07	-119.45	14.98	-613.817545	0.19
δ_L (g$^-$, g$^-$)	-90.07	-70.00	56.95	-177.07	175.33	-110.18	12.06	-613.814276	2.24
γ_L (g$^+$, g$^+$)	40.79	55.39	179.57	-174.51	175.92	-83.53	51.93	-613.811868	3.76
γ_L (g$^+$, a)	71.46	-177.88	-54.23	-176.28	-176.19	-85.50	74.23	-613.809372	5.32
γ_L (g$^+$, g$^-$)	39.22	-83.84	46.26	-177.73	176.96	-85.98	57.61	-613.806358	7.21
γ_L (a, g$^+$)	-174.73	57.88	-178.67	-178.07	-174.65	-84.50	80.34	-613.817369	0.30
γ_L (a, a)	-156.21	173.00	-62.89	-178.89	-172.42	-85.23	86.41	-613.815766	1.31
γ_L (a, g$^-$)	-157.20	-62.27	64.99	-178.40	-172.76	-84.78	85.02	-613.814380	2.18
γ_L (g$^-$, g$^+$)	-92.97	57.97	-177.65	-177.55	-175.85	-85.81	72.97	-613.815118	1.72
γ_L (g$^-$, a)	-69.52	164.51	-71.89	-178.94	-175.41	-84.90	76.62	-613.817239	0.39
γ_L (g$^-$, g$^-$)	-92.23	-70.99	55.95	-177.80	-176.11	-85.95	73.03	-613.813423	2.78
ε_L (g$^+$, g$^+$)						Not found			
ε_L (g$^+$, a)						Not found			

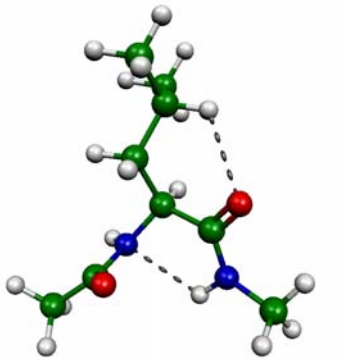
Final Geometry	χ_1 (7-8-13-14)	χ_2 (8-13-14-15)	χ_2' (8-13-14-17)	ω_0 (2-3-7-8)	ω_1 (8-9-26-27)	ϕ (3-7-8-9)	ψ (7-8-9-26)	Energy (Hartree)	$\Delta E_{rel.}$ (kcal.mol^{-1})
ε_L (g^+, g^-)						Not found			
ε_L (a, g^+)						Not found			
ε_L (a, a)						Not found			
ε_L (a, g^-)						Not found			
ε_L (g^-, g^+)	-88.36	59.69	-175.99	175.14	176.73	-118.46	138.65	-613.814667	2.00
ε_L (g^-, a)						Not found			
ε_L (g^-, g^-)	-88.68	-77.11	57.07	175.65	176.79	-118.14	135.32	-613.813516	2.72
α_L (g^+, g^+)						Not found			
α_L (g^+, a)						Not found			
α_L (g^+, g^-)						Not found			
α_L (a, g^+)						Not found			
α_L (a, a)						Not found			
α_L (a, g^-)	-170.76	-81.69	46.75	-174.41	179.12	-73.72	-32.89	-613.812278	3.50
α_L (g^-, g^+)						Not found			
α_L (g^-, a)						Not found			
α_L (g^-, g^-)						Not found			

[a] The global minimum corresponds to β_L (*g*$^-$, *a*) conformation having a total energy of -613.817853 hartree. This value is taken as reference value, corresponding to a relative energy 0.00 kcal mol^{-1}

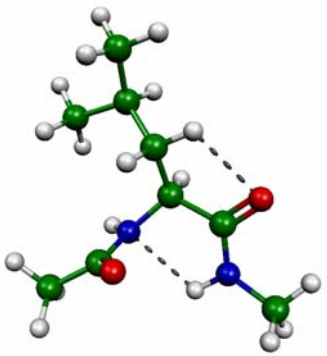
Figure S1: Conformers of $CH_3CO–Leu–NHCH_3$ optimized at B3LYP/6-31G(d) level of theory showing short distances (less or equal 2.5 Å).



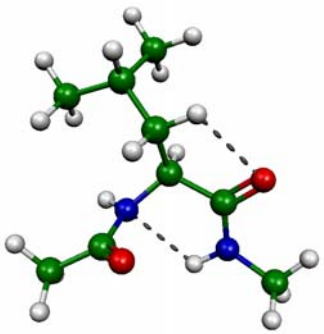
α_D (g^+, a)



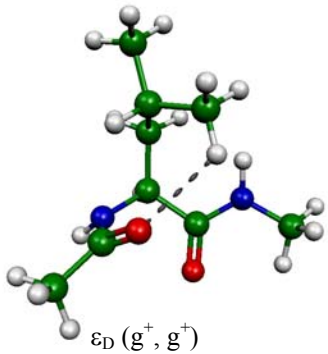
α_D (a, g^+)



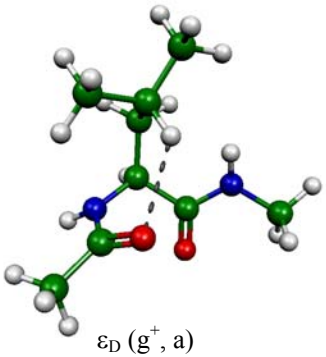
α_D (g^-, g^+)



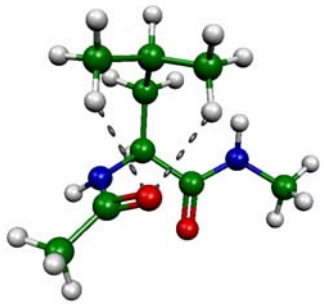
α_D (g^-, g^-)



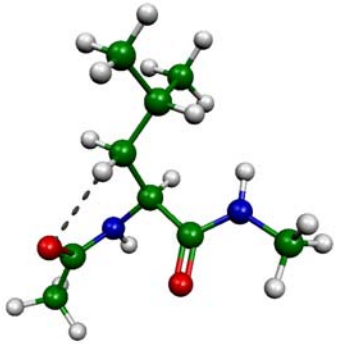
ε_D (g^+, g^+)



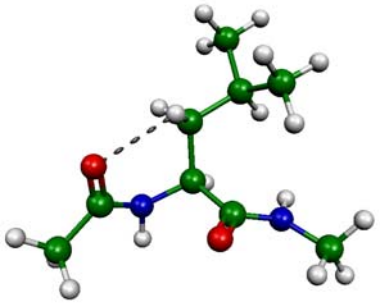
ε_D (g^+, a)



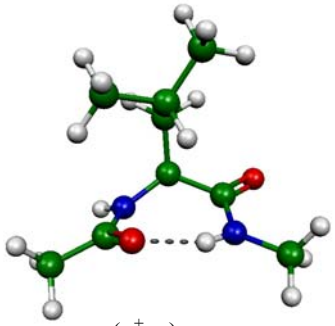
ε_D (g^+, g^-)



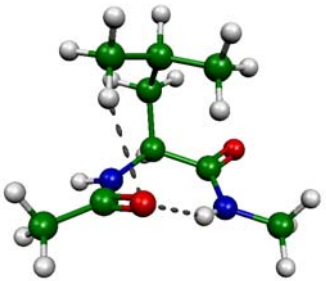
ε_D (a, g^+)



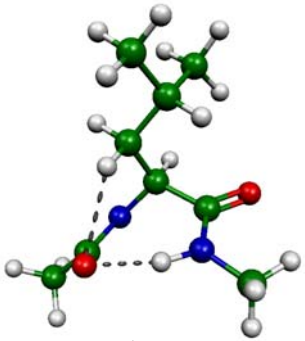
ε_D (a, a)



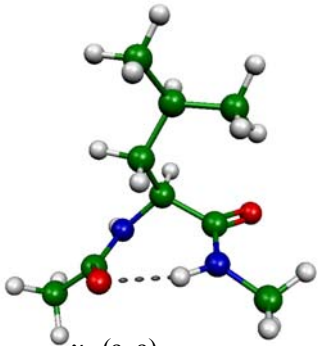
γ_D (g^+, a)



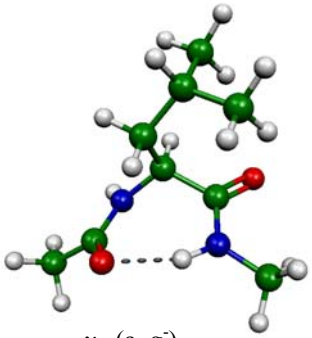
γ_D (g^+, g^-)



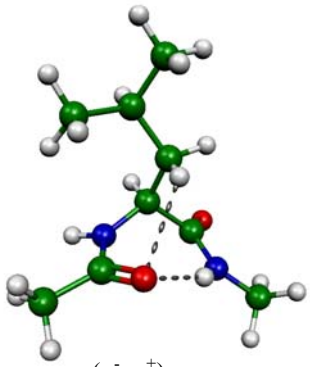
γ_D (a, g^+)



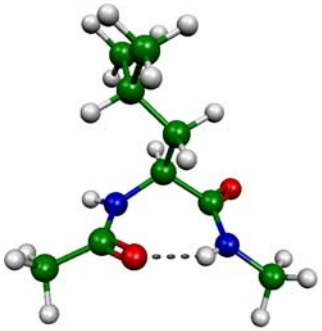
γ_D (a, a)



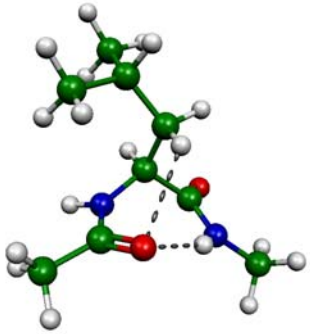
γ_D (a, g^-)



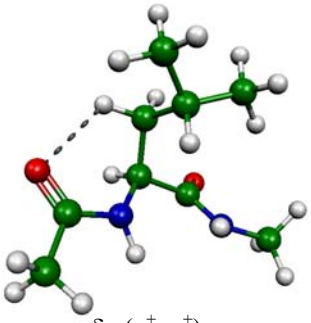
γ_D (g^-, g^+)



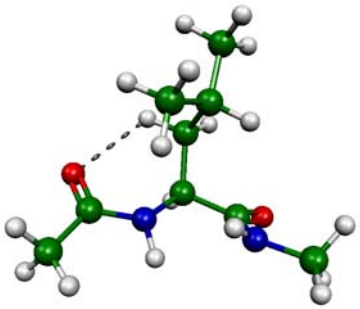
γ_D (g^-, a)



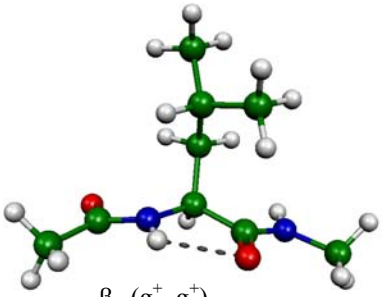
γ_D (g^-, g^-)



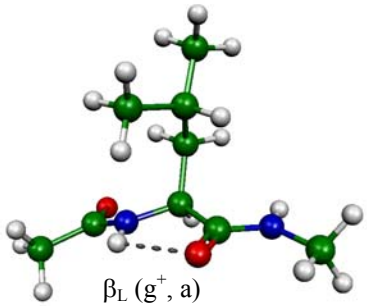
δ_D (g^+, g^+)



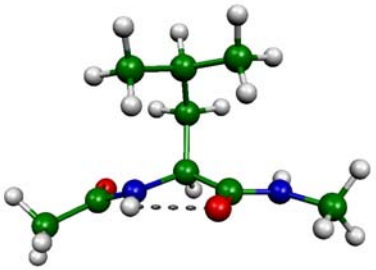
δ_D (g^+, a)



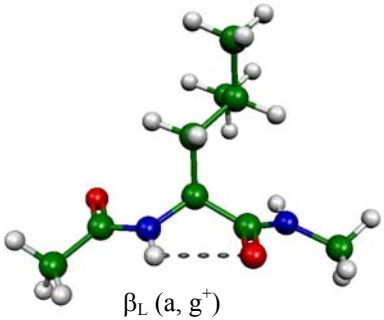
β_L (g^+, g^+)



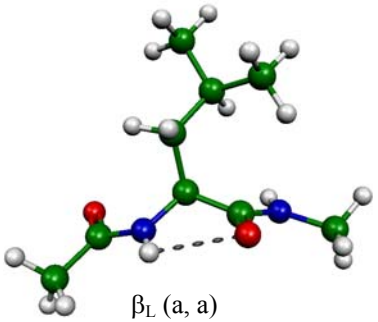
β_L (g^+, a)



β_L (g^+, g^-)



β_L (a, g^+)



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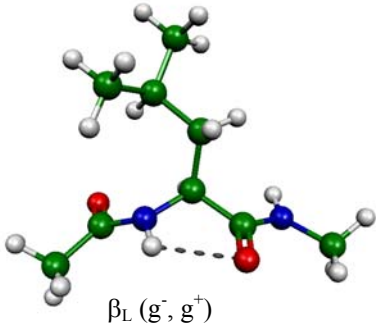
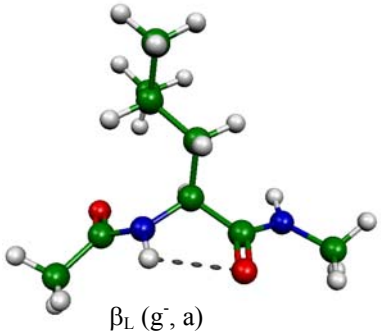


β_L (g^-, g^+)



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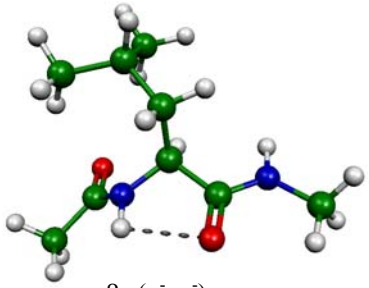
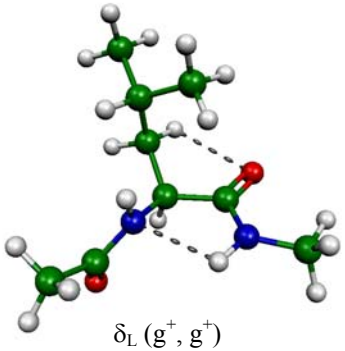


β_L (g^-, g^-)



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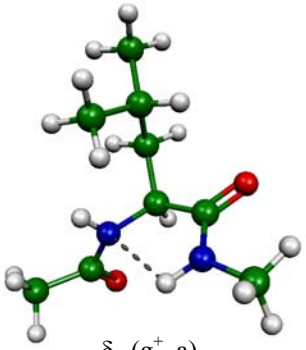

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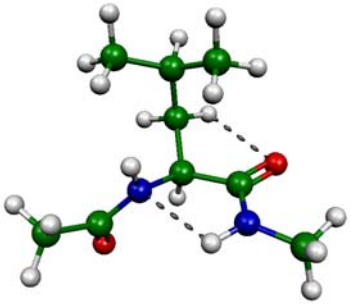

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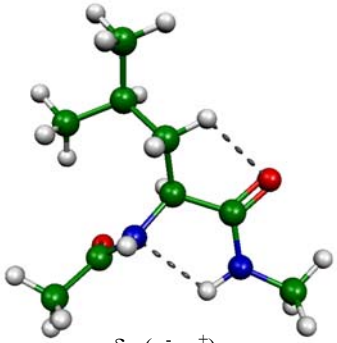

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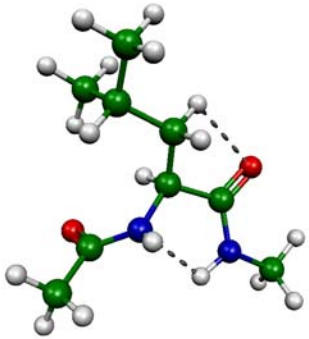

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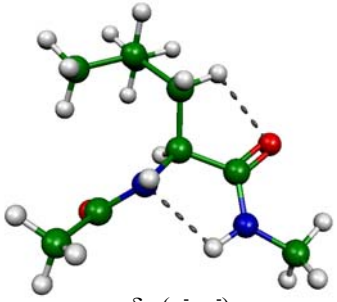
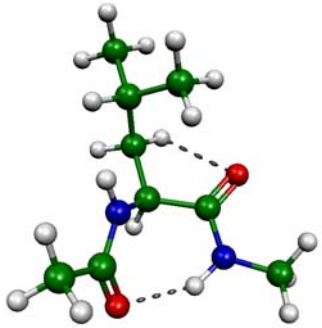
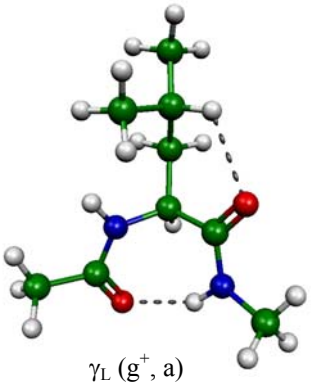


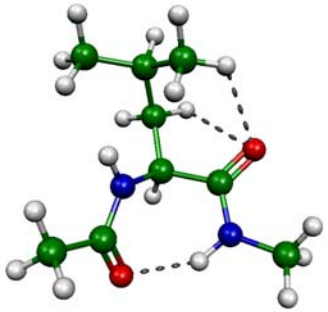
δ_L (g^-, g^-)



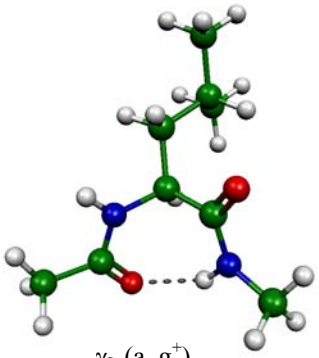
γ_L (g^+, g^+)



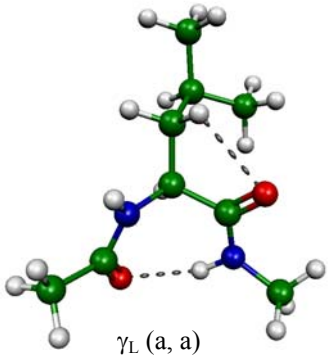
γ_L (g^+, a)



γ_L (g^+, g^-)



γ_L (a, g^+)



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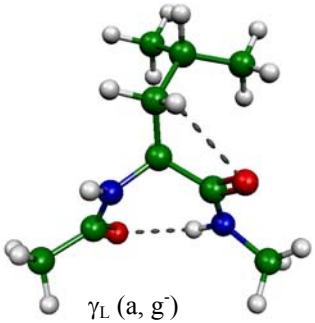

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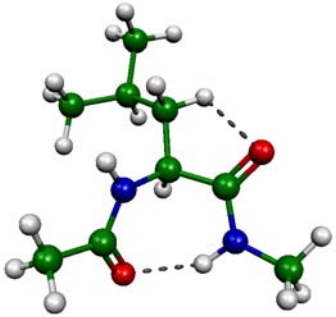
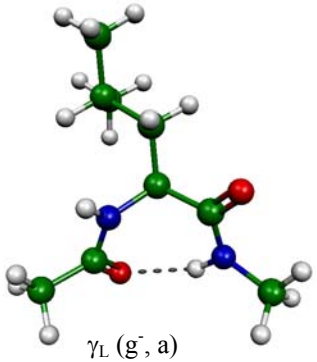
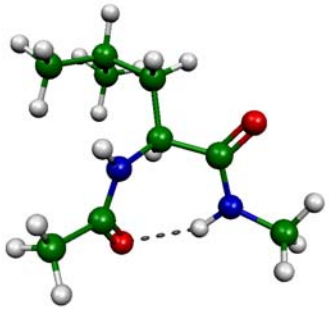


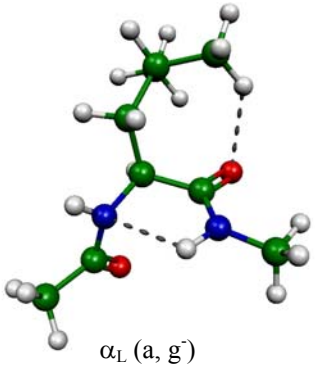
γ_L (g^-, g^+)



γ_L (g^-, a)

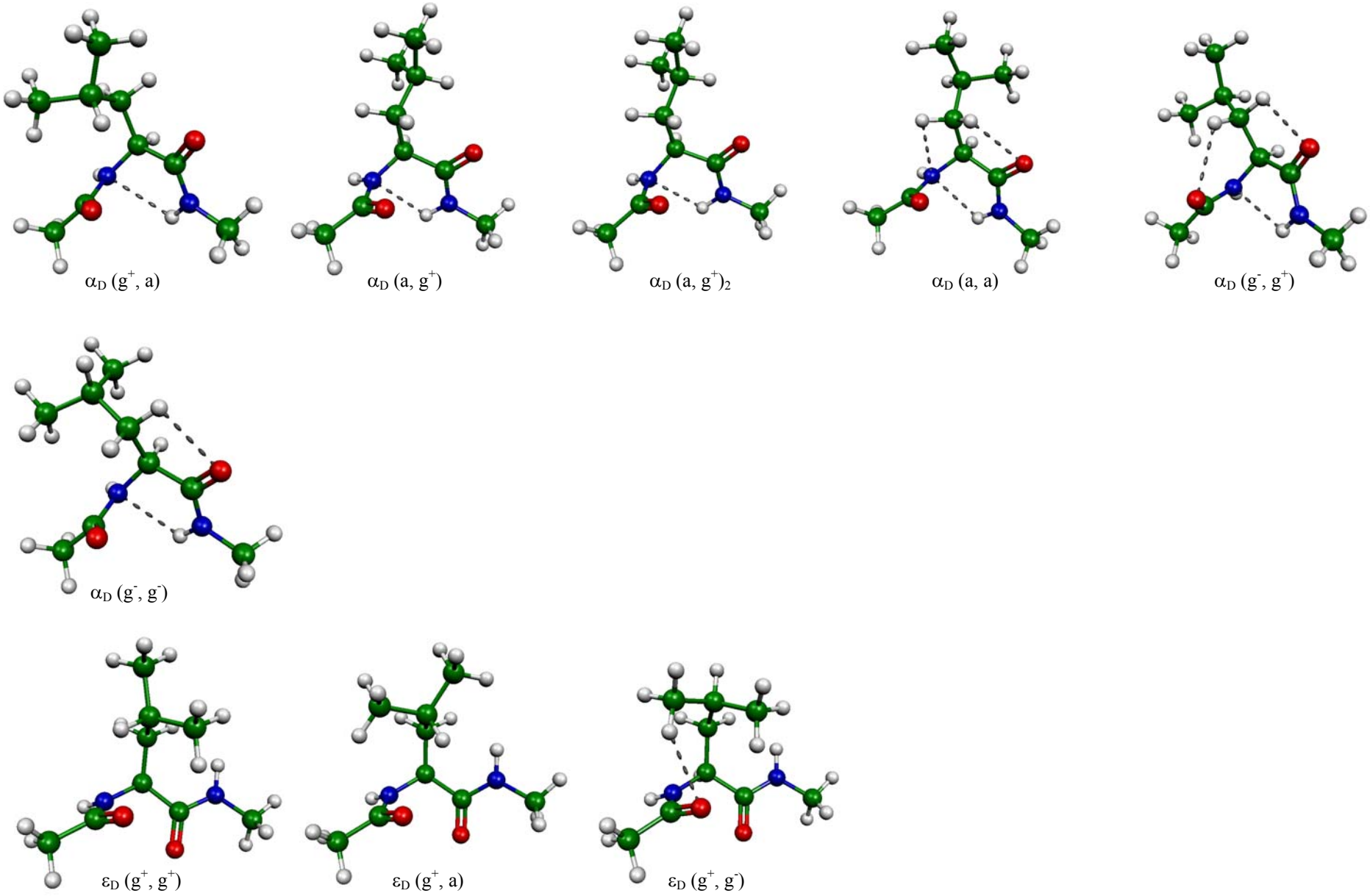


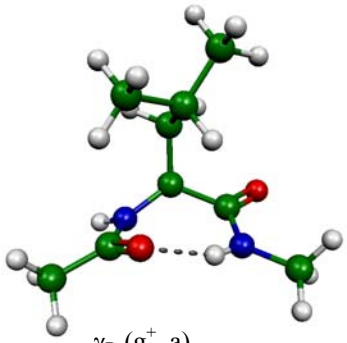
γ_L (g^-, g^-)



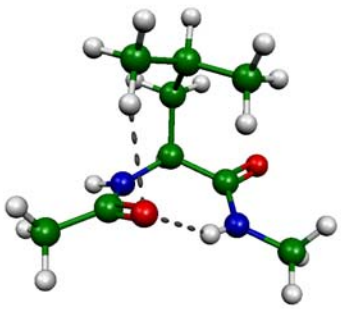
α_L (a, g^-)

Figure S2: Conformers of $CH_3CO–Leu–NHCH_3$ optimized at PB-SCRF/B3LYP/6-31G(d) level of theory using water (ε= 78.39) as solvent showing short distances (less or equal 2.5 Å).

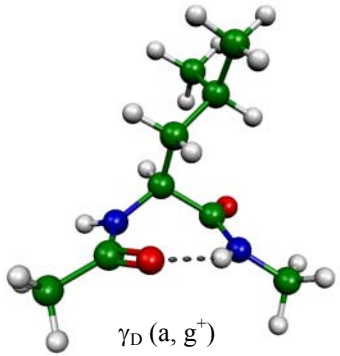




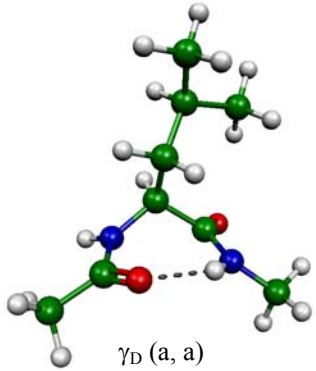
γ_D (g^+, a)



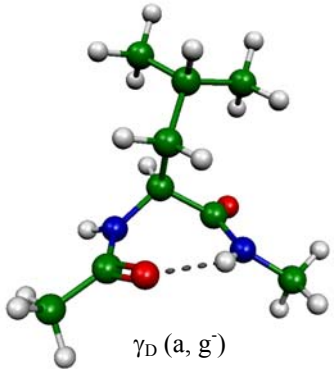
γ_D (g^+, g^-)



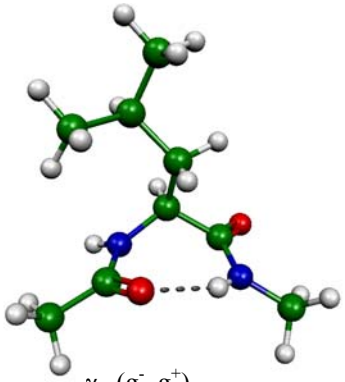
γ_D (a, g^+)



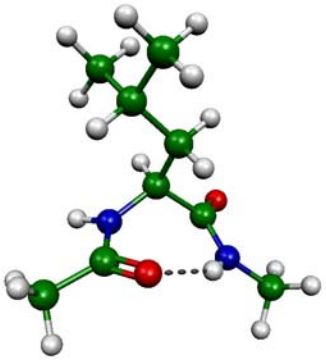
γ_D (a, a)



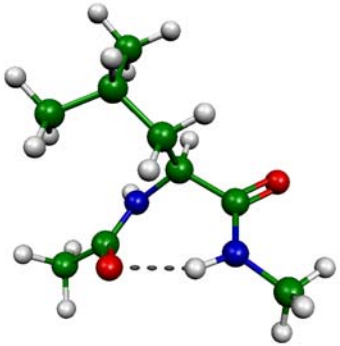
γ_D (a, g^-)



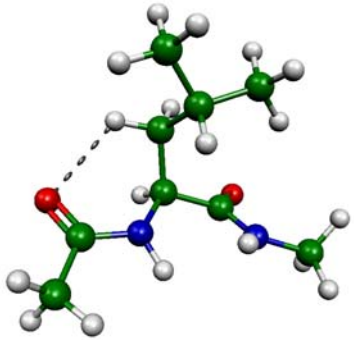
γ_D (g^-, g^+)



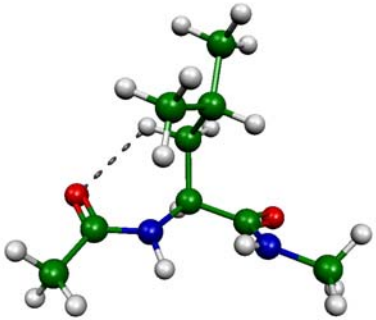
γ_D (g^-, a)



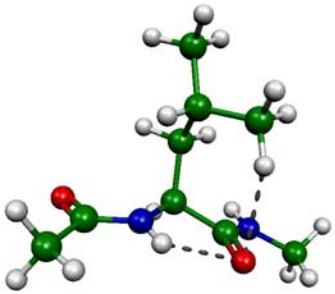
γ_D (g^-, g^-)



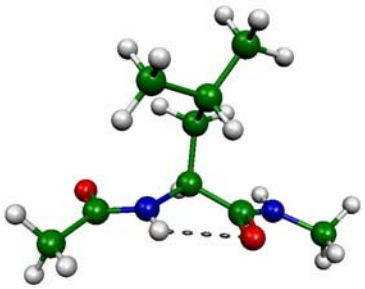
δ_D (g^+, g^+)



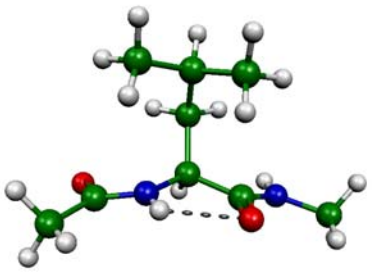
δ_D (g^+, a)



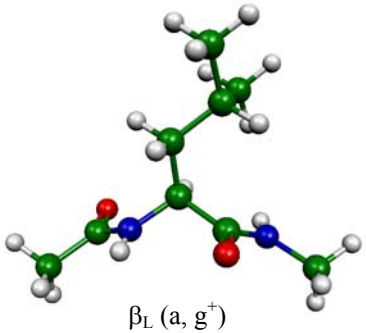
β_L (g^+, g^+)



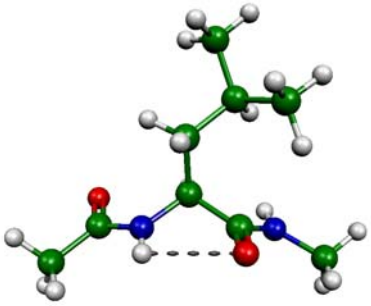
β_L (g^+, a)



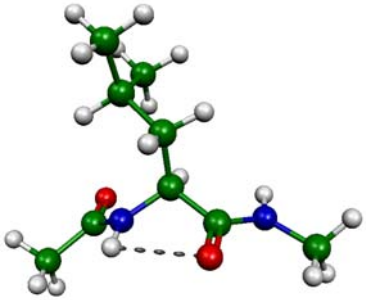
β_L (g^+, g^-)



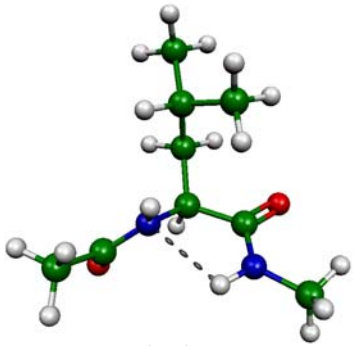
β_L (a, g^+)



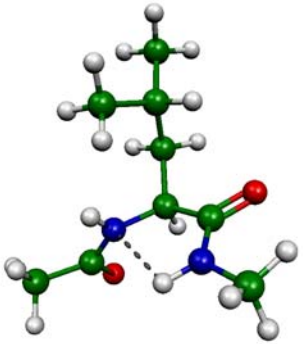
β_L (a, a)



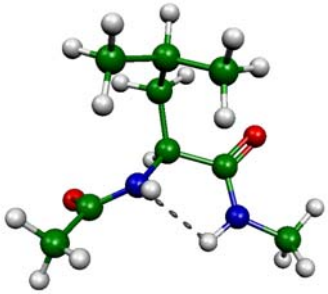
β_L (g^-, a)



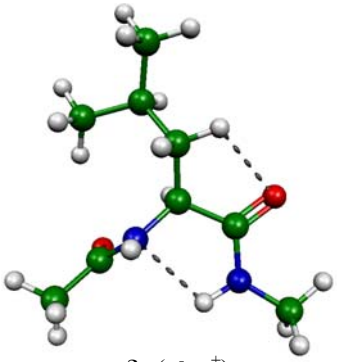
δ_L (g^+, g^+)



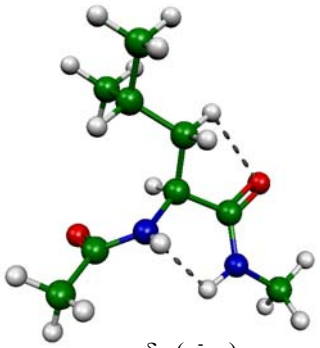
δ_L (g^+, a)



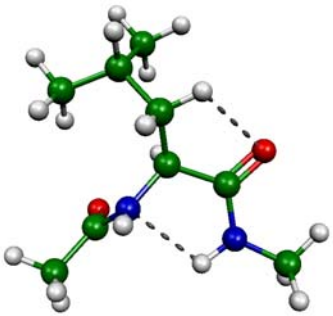
δ_L (g^+, g^-)



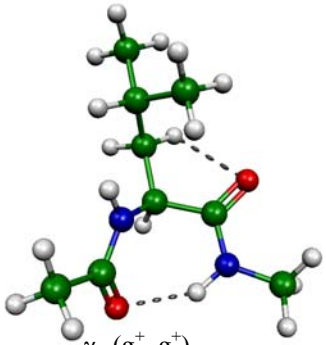
δ_L (g^-, g^+)



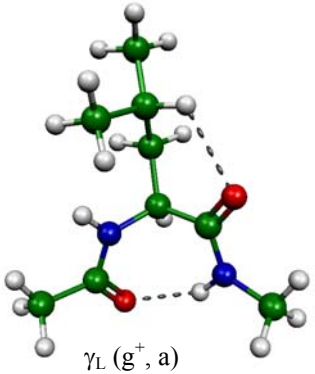
δ_L (g^-, a)



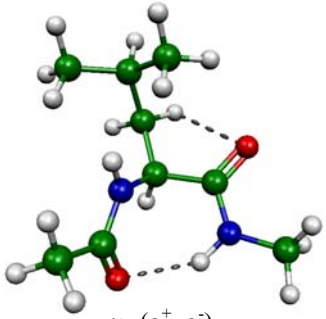
δ_L (g^-, g^-)



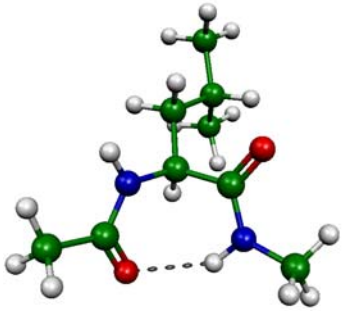
γ_L (g^+, g^+)



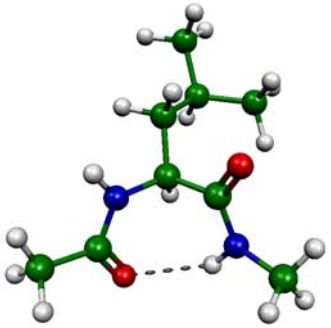
γ_L (g^+, a)



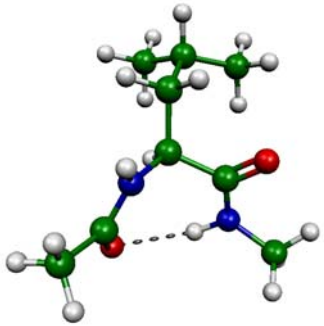
γ_L (g^+, g^-)



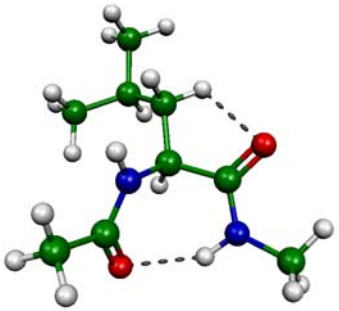
γ_L (a, g^+)



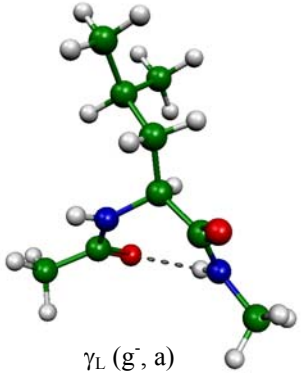
γ_L (a, a)



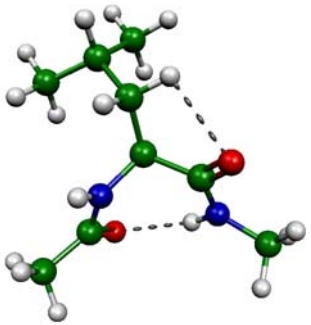
γ_L (a, g^-)



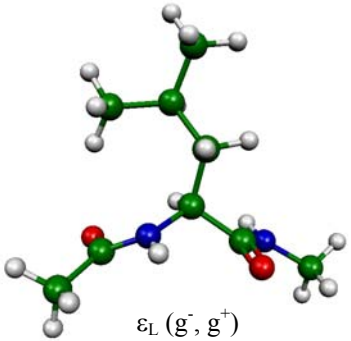
γ_L (g^-, g^+)



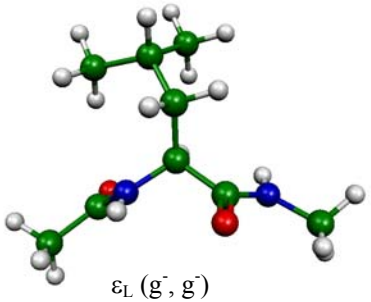
γ_L (g^-, a)



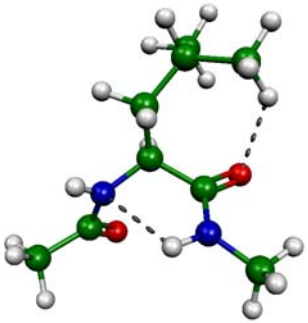
γ_L (g^-, g^-)



ε_L (g^-, g^+)



ε_L (g^-, g^-)



α_L (a, g^-)