Accurate quantum chemical energies for tetrapeptide conformations: Why MP2 data with an insufficient basis set should be handled with caution

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Electronic Supporting Information

14 pages

(contains technical details, statistical data, and relative and absolute energies for various theoretical approaches (Tables S1-S3) and structures of the tetrapeptide conformers (Tables S4-S5))

Technical Details

All MP2, SCS-MP2,[1] MP2-F12,[2] and CCSD(T)[3] calculations were carried out with MOLPRO 2010.1.[4] The convergence criterion for all SCF steps was set to 10^{-8} E_h. Density fitting/resolution-of-the-identity[5] (RI) approaches were used in the (SCS-)MP2 and MP2-F12 calculations.

Dunning's[6] correlation-consistent basis sets cc-pVDZ, cc-pVTZ and cc-pVQZ were employed, and will be abbreviated as VDZ, VTZ and VQZ in the following. Additional MP2 calculations were carried out at the double- and triple-ζ levels with the addition of diffuse functions from the respective augmented correlation-consistent Dunning sets to all non-hydrogen atoms (dubbed a′VDZ and a′VTZ in the following). MP2-F12 calculations were carried out with ansatz "3C(FIX)"[7] and geminal exponents β = 0.9 for VDZ-F12 and β = 1.0 for VTZ-F12.[8]

Extrapolations to the complete-basis-set (CBS) limit were carried out based on the MP2-F12 single-point energies by the two-point extrapolation scheme:[9]

$$E(CBS) = \frac{E(VXZ-F12)\,X^n - E(VYZ-F12)\,Y^n}{X^n - Y^n}. \qquad \text{(S1)}$$

X and *Y* represent the respective cardinal numbers of the applied basis sets (*X, Y* = 2 or 3 for VDZ-F12 and VTZ-F12). An exponent of $n = 3.087838$[10] was used to extrapolate the MP2-F12 energies. Alternative MP2/CBS values were obtained based on MP2/VTZ and MP2/VQZ energies (*X, Y* = 3 or 4). In that case, the HF and MP2 correlation energies were extrapolated separately with exponents of $n = 5$ and $n = 3$, respectively.[9] The relative conformational energies for the two tetrapeptides based on the two MP2/CBS schemes are shown in Table S1. In most cases, the energies are very similar to one another. However, in some cases deviations of up to 0.7 kJ mol^{-1} are observed. From previous studies,[10] it is more likely that the values based on MP2-F12 are closer to the 'true' CBS limit and therefore only those numbers are discussed in the main text and also used in the derivation of the estimated CCSD(T)/CBS values. These were obtained by using the approach of Jurečka and Hobza:[11]

$$E(CCSD(T)/CBS) \approx E(MP2/CBS) + E(CCSD(T)/VDZ) - E(MP2/VDZ). \qquad \text{(S2)}$$

Additional density functional theory (DFT) calculations were carried out with functionals that have been shown to be among the best methods for describing conformational energies.[12] These include B-LYP,[13,14] B3-LYP,[15,16] PW6B95,[17] M06-2X[18] and the double-hybrid DFT procedures B2-PLYP,[19] B2GP-PLYP,[20] PWPB95[21] and DSD-PBEP86.[22] M06-2X and DSD-PBEP86 calculations were carried out with Gaussian 09 Rev. C01,[23] while all the other DFT computations were performed with ORCA 2.9.[24] In all cases, the VQZ basis set was employed. Grimme's dispersion-correction DFT-D3[25]

combined with the Becke-Johnson damping formula[26] was applied by using the standalone program DFTD3.[27] As discussed in the literature, highly-parameterised functionals such as the Minnesota classes of functionals can also benefit from additional dispersion corrections.[12,28] For the sake of consistency we applied DFT-D3 also to M06-2X. However, instead of Becke-Johnson, so-called 'zero-damping' was applied.[12] The SCF convergence criterion in all cases was again set to 10^{-8} E_h. The largest ORCA quadrature grid "7" and Gaussian's "ultrafine" grid were used in the numerical integration to determine the exchange-correlation energies. All ORCA calculations were sped up with RI methods for the perturbative parts of the double-hybrids and the Coulomb part of the B-LYP functional. Calculation of exchange and Coulomb contributions in hybrid functionals and the hybrid parts of the double-hybrids was sped up by employing the RI method combined with Neese's "chain of spheres" approach (RIJCOSX).[29] The respective auxiliary basis sets were taken from ORCA's internal basis-set library.

Energies and statistical data for the various tetrapeptide conformers

Table S1 Relative energies (kJ mol^{-1}) for the two tetrapeptides with respect to each β_a conformer. Various wave function and dispersion-corrected density functional theory methods were tested, with various basis sets.

	ACE-ALA-GLY-ALA-NME					ACE-ALA-SER-ALA-NME				
	β_a	α_R	PP-II	α_L	β	β_a	α_R	PP-II	α_L	β
CCSD(T)/CBS[a]	0.0	2.4	4.4	8.0	8.5	0.0	4.4	11.0	7.5	11.1
CCSD(T)/VDZ	0.0	–13.1	–1.0	–11.2	7.5	0.0	–10.7	3.5	–11.4	9.9
MP2/CBS[b]	0.0	0.4	6.9	7.1	8.6	0.0	2.2	13.1	7.3	11.7
MP2/CBS[c]	0.0	0.0	6.8	6.5	9.1	0.0	1.7	12.7	6.6	12.0
MP2/VQZ	0.0	–2.2	6.2	4.4	8.7	0.0	–0.2	12.0	5.1	11.8
MP2/a′VTZ	0.0	–5.5	4.5	1.6	8.3	0.0	–3.6	10.6	1.9	11.2
MP2-F12/VTZ-F12	0.0	0.2	6.9	7.0	8.5	0.0	2.0	13.2	7.2	11.7
MP2/VTZ	0.0	–7.3	4.7	–0.8	8.1	0.0	–4.7	10.4	0.8	11.6
MP2/a′VDZ	0.0	–12.9	0.4	–6.1	7.0	0.0	–10.3	5.9	–5.4	10.4
MP2-F12/VDZ-F12	0.0	–0.1	7.1	6.7	8.4	0.0	1.7	13.4	6.9	11.5
MP2/VDZ	0.0	–15.1	1.4	–12.1	7.6	0.0	–12.9	5.6	–11.6	10.5
SCS-MP2/CBS[c]	0.0	6.5	6.8	13.5	9.1	0.0	7.9	12.7	13.2	11.2
SCS-MP2/VQZ	0.0	4.1	6.0	11.1	8.7	0.0	5.7	11.8	11.4	11.0
SCS-MP2/VTZ	0.0	–1.2	4.4	5.6	8.1	0.0	0.9	10.0	6.6	10.8
SCS-MP2/VDZ	0.0	–10.6	0.6	–7.5	7.8	0.0	–8.8	4.6	–7.7	9.9
HF/CBS[d]	0.0	34.6	6.8	44.0	11.7	0.0	34.8	13.7	42.6	11.0
HF/VQZ	0.0	33.5	6.4	42.7	11.7	0.0	33.9	13.3	41.4	11.1
HF/VTZ	0.0	30.1	5.4	38.5	11.6	0.0	30.9	12.0	37.4	11.4
HF/VDZ	0.0	17.2	1.4	20.9	11.2	0.0	19.0	7.3	18.6	1.3
B-LYP-D3/VQZ	0.0	0.5	7.8	7.6	5.4	0.0	3.5	14.3	10.0	9.1
B3-LYP-D3/VQZ	0.0	3.5	7.8	10.4	7.8	0.0	6.0	14.2	11.4	10.8
PW6B95-D3/VQZ	0.0	5.7	9.7	10.1	8.8	0.0	6.9	15.8	8.5	11.9
M06-2X-D3/VQZ	0.0	–1.0	5.7	3.1	11.4	0.0	–0.4	10.6	0.5	13.6
B2-PLYP-D3/VQZ	0.0	4.0	7.6	10.7	8.3	0.0	6.8	14.8	11.7	11.5
B2GP-PLYP-D3/VQZ	0.0	4.7	7.5	11.2	8.8	0.0	7.6	15.0	12.1	12.3
PWPB95-D3/VQZ	0.0	4.5	8.4	9.1	8.9	0.0	6.0	15.0	7.6	12.2
DSD-PBEP86-D3/VQZ	0.0	2.3	6.3	8.6	8.4	0.0	4.2	12.4	8.8	16.1

[a] MP2-F12/V{D,T}Z-F12 corrected for difference between CCSD(T)/VDZ and MP2/VDZ. [b] MP2-F12/V{D,T}Z-F12 result obtained as described in technical details. [c] (SCS-)MP2/V{T,Q}Z results obtained with exponents of $n = 5$ for the extrapolation of HF energies and of $n = 3$ for the extrapolation of the (SCS-)MP2 correlation energies. [d] HF/V{T,Q}Z results obtained with extrapolation exponent of $n = 5$.

Table S2 Mean deviations (MDs), mean absolute deviations (MADs) and root-mean-square deviations (RMSDs) (kJ mol^{-1}) for various wave function and density functional theory methods. The numbers were calculated with respect to the estimated CCSD(T)/CBS reference values for the two tetrapeptides.

	MD	MAD	RMSD
CCSD(T)/VDZ	–10.5	10.5	12.7
MP2/CBS[a]	0.0	1.3	1.6
MP2/VQZ	–1.4	2.4	2.9
MP2/a′VTZ	–3.5	3.6	5.0
MP2-F12/VTZ-F12	–0.1	1.4	1.7
MP2/VTZ	–4.3	4.5	6.1
MP2/a′VDZ	–8.5	8.5	10.4
MP2-F12/VDZ-F12	–0.2	1.6	1.9
MP2/VDZ	–10.5	10.5	13.3
SCS-MP2/CBS[b]	3.0	3.0	3.6
SCS-MP2/VQZ	1.6	1.6	2.0
SCS-MP2/VTZ	–1.5	1.5	2.0
SCS-MP2/VDZ	–8.6	8.6	10.4
HF/CBS[c]	17.7	17.8	23.7
HF/VQZ	17.1	17.1	22.9
HF/VTZ	15.0	15.0	20.3
HF/VDZ	5.0	9.1	10.3
B-LYP-D3/VQZ	0.1	2.2	2.4
B3-LYP-D3/VQZ	1.8	2.1	2.4
PW6B95-D3/VQZ	2.5	2.5	3.0
M06-2X-D3/VQZ	–1.7	3.4	3.9
B2-PLYP-D3/VQZ	2.3	2.3	2.7
B2GP-PLYP-D3/VQZ	2.7	2.7	3.0
PWPB95-D3/VQZ	1.8	1.8	2.3
DSD-PBEP86-D3/VQZ	1.2	1.3	2.0

[a] MP2-F12/V{D,T}Z-F12 result obtained as described in technical details. [b] SCS-MP2/V{T,Q}Z results obtained with exponents of $n = 5$ for the extrapolation of HF energies and of $n = 3$ for the extrapolation of the SCS-MP2 correlation energies. [d] HF/V{T,Q}Z results obtained with extrapolation exponent of $n = 5$.

Table S3 Absolute energies (E_h) for all considered conformers of the two tetrapeptides. Results are shown for various wave function and dispersion-corrected density functional theory methods.

	ACE-ALA-GLY-ALA-NME					ACE-ALA-SER-ALA-NME				
	β_a	α_R	PP-II	α_L	β	β_a	α_R	PP-II	α_L	β
CCSD(T)/CBS[a]	–950.21392	–950.21301	–950.21223	–950.21086	–950.21069	–1064.64617	–1064.64450	–1064.64200	–1064.64331	–1064.64194
CCSD(T)/VDZ	–948.71975	–948.72473	–948.72013	–948.72401	–948.71689	–1062.96768	–1062.97176	–1062.96636	–1062.97203	–1062.96390
MP2/CBS[b]	–949.97990	–949.97976	–949.97729	–949.97719	–949.97663	–1064.38979	–1064.38896	–1064.38479	–1064.38701	–1064.38533
MP2/CBS[c]	–949.94973	–949.94973	–949.94714	–949.94726	–949.94627	–1064.35575	–1064.35509	–1064.35092	–1064.35324	–1064.35118
MP2/VQZ	–949.75008	–949.75093	–949.74773	–949.74839	–949.74677	–1064.13189	–1064.13199	–1064.12731	–1064.12994	–1064.12741
MP2/a′VTZ	–949.50887	–949.51095	–949.50714	–949.50825	–949.50572	–1063.86252	–1063.86388	–1063.85848	–1063.86179	–1063.85825
MP2-F12/VTZ-F12	–949.94770	–949.94761	–949.94507	–949.94504	–949.94445	–1064.35333	–1064.35255	–1064.34830	–1064.35059	–1064.34889
MP2/VTZ	–949.43847	–949.44124	–949.43669	–949.43878	–949.43539	–1063.78247	–1063.78426	–1063.77852	–1063.78217	–1063.77805
MP2/a′VDZ	–948.67655	–948.68145	–948.67669	–948.67888	–948.67387	–1062.93256	–1062.93647	–1062.93033	–1062.93461	–1062.92860
MP2-F12/VDZ-F12	–949.86728	–949.86733	–949.86459	–949.86475	–949.86408	–1064.26227	–1064.26164	–1064.25718	–1064.25966	–1064.25789
MP2/VDZ	–948.48574	–948.49148	–948.48520	–948.49033	–948.48284	–1062.71130	–1062.71622	–1062.70915	–1062.71572	–1062.70729
SCS-MP2/CBS[c]	–949.92343	–949.92093	–949.92083	–949.91830	–949.91997	–1064.32452	–1064.32153	–1064.31969	–1064.31951	–1064.32025
SCS-MP2/VQZ	–949.70964	–949.70808	–949.70735	–949.70540	–949.70633	–1064.08492	–1064.08276	–1064.08041	–1064.08059	–1064.08074
SCS-MP2/VTZ	–949.37867	–949.37913	–949.37701	–949.37655	–949.37557	–1063.71393	–1063.71357	–1063.71014	–1063.71140	–1063.70981
SCS-MP2/VDZ	–948.41221	–948.41623	–948.41198	–948.41505	–948.40922	–1062.62814	–1062.63148	–1062.62638	–1062.63106	–1062.62436
HF/CBS[d]	–945.95236	–945.93919	–945.94979	–945.93560	–945.94790	–1059.89532	–1059.88205	–1059.89011	–1059.87907	–1059.89114
HF/VQZ	–945.93174	–945.91898	–945.92929	–945.91548	–945.92729	–1059.87218	–1059.85928	–1059.86713	–1059.85641	–1059.86797
HF/VTZ	–945.86547	–945.85402	–945.86343	–945.85081	–945.86105	–1059.79783	–1059.78607	–1059.79324	–1059.78357	–1059.79349
HF/VDZ	–945.60079	–945.59424	–945.60024	–945.59284	–945.59651	–1059.49931	–1059.49209	–1059.49653	–1059.49223	–1059.49501
B-LYP-D3/VQZ	–951.39458	–951.39440	–951.39160	–951.39169	–951.39252	–1065.95585	–1065.95453	–1065.95040	–1065.95204	–1065.95239
B3-LYP-D3/VQZ	–951.16000	–951.15865	–951.15703	–951.15604	–951.15702	–1065.69234	–1065.69007	–1065.68694	–1065.68799	–1065.68825
PW6B95-D3/VQZ	–952.78220	–952.78003	–952.77851	–952.77835	–952.77885	–1067.50040	–1067.49777	–1067.49440	–1067.49718	–1067.49588
M06-2X-D3/VQZ	–951.22728	–951.22766	–951.22511	–951.22608	–951.22295	–1065.76815	–1065.76832	–1065.76411	–1065.76794	–1065.76297
B2-PLYP-D3/VQZ	–951.13168	–951.13017	–951.12877	–951.12761	–951.12851	–1065.66199	–1065.65941	–1065.65637	–1065.65754	–1065.65762
B2GP-PLYP-D3/VQZ	–951.01299	–951.01120	–951.01014	–951.00872	–951.00965	–1065.53008	–1065.52717	–1065.52435	–1065.52549	–1065.52538
PWPB95-D3/VQZ	–951.15543	–951.15373	–951.15224	–951.15198	–951.15205	–1065.68821	–1065.68594	–1065.68251	–1065.68533	–1065.68358
DSD-PBEP86-D3/VQZ	–950.08138	–950.08051	–950.07897	–950.07810	–950.07817	–1064.49384	–1064.49225	–1064.48912	–1064.49048	–1064.48770

[a] MP2-F12/V{D,T}Z-F12 corrected for difference between CCSD(T)/VDZ and MP2/VDZ. [b] MP2-F12/V{D,T}Z-F12 result obtained as described in technical details. [c] (SCS-)MP2/V{T,Q}Z results obtained with exponents of $n = 5$ for the extrapolation of HF energies and of $n = 3$ for the extrapolation of the (SCS-)MP2 correlation energies. [d] HF/V{T,Q}Z results obtained with extrapolation exponent of $n = 5$.

Geometries for conformers of the two tetrapeptides

Backbone geometries are usually described by the dihedral angles ϕ (C-N-Cα-C) and ψ (N-Cα-C-N). The dihedrals for the five tested conformations are:

- ϕ = –140° and ψ = 135° for the β_a conformer,
- ϕ = –57° and ψ = –47° for the α_R conformer,
- ϕ = –79° and ψ = 150° for the PP-II conformer,
- ϕ = 57° and ψ = 47° for the α_L conformer, and
- ϕ = –119° and ψ = 113° for the β conformer.

The Cartesian coordinates (Å) of all 10 conformers are given below. All structures were taken from ref. 30.

Table S4 Geometric structures (Å) of the five conformers of ACE-ALA-GLY-ALA-NME.

β_a conformer				α_R conformer			
H	-7.569044	-0.937848	-0.872932	H	-1.902834	3.364174	-1.576849
C	-6.756047	-1.135862	-0.174932	C	-2.612847	3.049204	-0.807849
H	-6.406065	-2.164868	-0.309932	H	-3.607851	2.954245	-1.249849
H	-7.129046	-1.042856	0.850068	H	-2.637814	3.835205	-0.046849
C	-5.636030	-0.138882	-0.438932	C	-2.106900	1.770183	-0.168849
O	-5.707015	0.728120	-1.302932	O	-0.929905	1.631134	0.163151
N	-4.543032	-0.283901	0.368068	N	-3.027941	0.773221	-0.001849
H	-4.479045	-1.036902	1.041068	H	-3.996931	1.002261	-0.176849
C	-3.352018	0.539079	0.228068	C	-2.770989	-0.400790	0.842151
H	-3.371011	0.944079	-0.787932	H	-2.545976	-0.075799	1.864151
C	-3.321998	1.699078	1.238068	C	-3.999027	-1.314739	0.852151
H	-3.319005	1.309078	2.260068	H	-4.240042	-1.671729	-0.153849
H	-2.427987	2.316063	1.098068	H	-3.803063	-2.182747	1.486151
H	-4.203987	2.328094	1.097068	H	-4.872005	-0.791703	1.258151
C	-2.145034	-0.381942	0.439068	C	-1.510021	-1.173842	0.410151
O	-2.126048	-1.190943	1.366068	O	-0.729039	-1.608874	1.243151
N	-1.129032	-0.238960	-0.448932	N	-1.397031	-1.425846	-0.922849
H	-1.175020	0.443041	-1.193932	H	-2.033012	-0.957820	-1.551849
C	0.117956	-0.970981	-0.335932	C	-0.258062	-2.156893	-1.465849
H	0.184949	-1.366983	0.680068	H	-0.231104	-3.170895	-1.060849
H	0.141941	-1.821982	-1.030932	H	-0.380064	-2.215888	-2.550849
C	1.265972	-0.028001	-0.698932	C	1.123964	-1.546951	-1.151849
O	1.172985	0.717000	-1.672932	O	2.071934	-2.268990	-0.892849
N	2.340972	-0.059020	0.123068	N	1.231019	-0.197955	-1.361849
H	2.390960	-0.699021	0.906068	H	0.374041	0.340080	-1.298849
C	3.544985	0.723959	-0.126932	C	2.460049	0.516994	-1.001849
H	3.538990	0.976959	-1.190932	H	3.283029	0.049960	-1.545849
C	3.573008	2.013959	0.707068	C	2.337110	1.989999	-1.397849
H	3.565003	1.773959	1.774068	H	1.502129	2.468034	-0.875849
H	4.473018	2.597943	0.491068	H	3.257131	2.518961	-1.132849
H	2.697018	2.623974	0.471068	H	2.181114	2.087006	-2.476849
C	4.735970	-0.175062	0.235068	C	2.874043	0.376977	0.483151
O	4.727958	-0.836062	1.270068	O	4.054037	0.223929	0.779151
N	5.767969	-0.190080	-0.642932	N	1.876051	0.570018	1.389151
H	5.701979	0.348922	-1.491932	H	0.920052	0.600058	1.062151
C	6.965956	-0.977100	-0.387932	C	2.089043	0.386010	2.813151
H	6.715937	-2.037096	-0.278932	H	3.158037	0.235966	2.971151
H	7.654958	-0.854112	-1.224932	H	1.764080	1.269023	3.376151
H	7.457961	-0.651109	0.534068	H	1.542007	-0.488968	3.181151

Table S4 *continued*

PP-II conformer				α_L conformer			
H	7.170034	0.869937	-0.530959	H	2.312973	-1.374089	3.345925
C	6.277036	1.076944	0.059041	C	3.070973	-1.369112	2.559925
H	5.900044	2.065947	-0.224959	H	3.369942	-2.407121	2.385925
H	6.532036	1.099942	1.122041	H	3.943990	-0.805138	2.897925
C	5.222028	0.031952	-0.262959	C	2.451989	-0.821093	1.286925
O	5.179023	-0.554048	-1.335959	O	1.306981	-1.111059	0.945925
N	4.326026	-0.223041	0.757041	N	3.236015	0.036883	0.560925
H	4.233031	0.509960	1.450041	H	4.205017	0.103855	0.837925
C	3.083020	-0.914031	0.456041	C	2.944025	0.383892	-0.842075
H	3.329014	-1.693033	-0.270959	H	3.644049	1.189871	-1.095075
C	2.484015	-1.531026	1.729041	C	3.150990	-0.790114	-1.799075
H	2.301021	-0.754025	2.479041	H	2.477966	-1.611094	-1.544075
H	1.525012	-2.010019	1.516041	H	2.929999	-0.480107	-2.822075
H	3.171009	-2.270032	2.151041	H	4.184980	-1.144145	-1.748075
C	2.065028	0.059977	-0.164959	C	1.525043	0.981934	-0.990075
O	2.041037	1.246977	0.138041	O	0.785034	0.667956	-1.910075
N	1.178023	-0.506016	-1.040959	N	1.210071	1.946944	-0.082075
H	1.143015	-1.516016	-1.063959	H	1.844076	2.100925	0.687925
C	-0.061971	0.171994	-1.351959	C	-0.080908	2.622982	-0.097075
H	0.160037	1.231992	-1.495959	H	-0.099887	3.332982	0.733925
H	-0.472974	-0.226003	-2.286959	H	-0.210892	3.174986	-1.031075
C	-1.106973	-0.018998	-0.241959	C	-1.310936	1.696018	0.009925
O	-1.116981	-1.021998	0.462041	O	-2.309929	1.927048	-0.652075
N	-1.993965	1.012009	-0.094959	N	-1.236964	0.746016	0.989925
H	-2.070960	1.655010	-0.872959	H	-0.308972	0.476989	1.289925
C	-3.222966	0.812019	0.657041	C	-2.299994	-0.248952	1.198925
H	-2.958971	0.193017	1.519041	H	-1.892014	-0.946964	1.940925
C	-3.788956	2.160023	1.122041	C	-3.578975	0.378086	1.752925
H	-4.052951	2.783025	0.260041	H	-3.993954	1.083098	1.032925
H	-4.693957	2.014030	1.717041	H	-4.320998	-0.400892	1.934925
H	-3.050951	2.693017	1.727041	H	-3.362960	0.899079	2.690925
C	-4.255972	0.076027	-0.222959	C	-2.594019	-1.095944	-0.069075
O	-4.301970	0.268027	-1.432959	O	-3.741027	-1.374910	-0.399075
N	-5.132978	-0.714966	0.455041	N	-1.485033	-1.584976	-0.691075
H	-4.940980	-0.916968	1.425041	H	-0.580023	-1.232003	-0.414075
C	-6.181984	-1.467958	-0.213959	C	-1.568055	-2.301974	-1.950075
H	-5.954993	-2.539960	-0.239959	H	-1.128037	-1.715987	-2.764075
H	-7.142983	-1.320950	0.288041	H	-1.050083	-3.265989	-1.887075
H	-6.246981	-1.097957	-1.236959	H	-2.623060	-2.478943	-2.162075

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Table S4 *continued*

β conformer			
H	-6.373048	-2.115944	0.936000
C	-6.407027	-1.030943	0.811000
H	-6.364018	-0.555944	1.795000
H	-7.362022	-0.786924	0.339000
C	-5.283019	-0.611965	-0.123000
O	-5.193027	-1.046967	-1.265000
N	-4.394001	0.289017	0.399000
H	-4.447996	0.549019	1.374000
C	-3.221992	0.749995	-0.335000
H	-3.258002	0.229995	-1.295000
C	-3.242962	2.266995	-0.548000
H	-3.200952	2.783994	0.415000
H	-2.379956	2.585978	-1.141000
H	-4.154957	2.559013	-1.075000
C	-1.982000	0.342970	0.477000
O	-1.774991	0.820966	1.590000
N	-1.183019	-0.597045	-0.097000
H	-1.383025	-0.928041	-1.031000
C	0.035972	-1.076069	0.531000
H	0.092981	-0.602070	1.512000
H	-0.005049	-2.164068	0.661000
C	1.232978	-0.760093	-0.372000
O	1.327968	-1.280094	-1.481000
N	2.112996	0.154890	0.115000
H	2.008003	0.509892	1.055000
C	3.309004	0.567867	-0.616000
H	3.287993	0.000867	-1.550000
C	3.299034	2.072867	-0.904000
H	3.330045	2.633866	0.033000
H	4.176039	2.354850	-1.496000
H	2.399039	2.345885	-1.461000
C	4.526997	0.196843	0.246000
O	4.715008	0.747839	1.326000
N	5.328978	-0.778173	-0.261000
H	5.060969	-1.216168	-1.130000
C	6.491968	-1.283196	0.448000
H	6.353948	-2.328193	0.749000
H	7.390969	-1.211213	-0.173000
H	6.620980	-0.671198	1.341000

Table S5 Geometric structures (Å) of the five conformers of ACE-ALA-SER-ALA-NME.

β_a conformer				α_R conformer			
H	7.073917	1.644016	-0.555080	H	-1.648188	-2.477936	3.123037
C	6.852928	0.847013	0.158920	C	-2.260205	-2.791904	2.276037
H	6.658922	1.288010	1.140920	H	-3.314195	-2.608847	2.501037
H	7.739936	0.211024	0.223920	H	-2.110263	-3.868912	2.146037
C	5.696938	0.016998	-0.380080	C	-1.772167	-2.078930	1.028037
O	5.740945	-0.518001	-1.484080	O	-0.575161	-1.970994	0.766037
N	4.619939	-0.094016	0.449920	N	-2.739138	-1.543878	0.223037
H	4.580933	0.390984	1.335920	H	-3.701151	-1.781826	0.425037
C	3.414949	-0.814031	0.071920	C	-2.445113	-1.077894	-1.135963
H	3.413949	-0.869031	-1.021080	H	-2.025157	-1.899916	-1.725963
C	3.379967	-2.237031	0.654920	C	-3.724086	-0.565825	-1.803963
H	3.395966	-2.199031	1.747920	H	-4.163041	0.270198	-1.248963
H	2.474973	-2.767043	0.338920	H	-3.498067	-0.222837	-2.815963
H	4.249974	-2.796020	0.302920	H	-4.471129	-1.363785	-1.877963
C	2.224938	0.002954	0.589920	C	-1.337056	-0.006953	-1.151963
O	2.233932	0.476954	1.724920	O	-0.429059	-0.060002	-1.970963
N	1.194936	0.165941	-0.280080	N	-1.464002	0.996054	-0.241963
H	1.204942	-0.271059	-1.193080	H	-2.322998	1.071100	0.287037
C	-0.058072	0.800925	0.092920	C	-0.569940	2.149006	-0.226963
H	-0.136072	0.776924	1.182920	H	-0.634910	2.708009	-1.164963
C	-0.092090	2.264925	-0.365080	C	-0.949891	3.065026	0.932037
H	0.750903	2.789935	0.105920	H	-0.939922	2.495026	1.874037
H	0.039909	2.296926	-1.456080	H	-0.190849	3.854986	1.003037
O	-1.348097	2.794909	0.034920	O	-2.239863	3.601095	0.651037
H	-1.383109	3.722908	-0.225080	H	-2.470830	4.216108	1.358037
C	-1.184062	0.001911	-0.579080	C	0.915038	1.736926	-0.085963
O	-1.058057	-0.372087	-1.747080	O	1.787070	2.337880	-0.691963
N	-2.255058	-0.288103	0.191920	N	1.162988	0.813913	0.894037
H	-2.358063	0.123896	1.110920	H	0.392955	0.198954	1.138037
C	-3.428049	-0.976118	-0.331080	C	2.509959	0.274841	1.100037
H	-3.412051	-0.847117	-1.418080	H	3.176004	1.116805	1.300037
C	-3.408030	-2.475117	0.007920	C	2.502908	-0.686159	2.292037
H	-3.410029	-2.614117	1.091920	H	1.818863	-1.523122	2.116037
H	-4.285024	-2.980128	-0.410080	H	3.507886	-1.087213	2.446037
H	-2.509025	-2.934106	-0.411080	H	2.194936	-0.165142	3.205037
C	-4.656058	-0.304133	0.299920	C	3.135923	-0.400193	-0.143963
O	-4.677061	-0.054133	1.501920	O	4.323932	-0.234256	-0.395963
N	-5.679061	-0.029146	-0.551080	N	2.326876	-1.273149	-0.806963
H	-5.556059	-0.232144	-1.532080	H	1.333878	-1.246096	-0.620963
C	-6.928069	0.569838	-0.109080	C	2.748842	-1.916172	-2.038963
H	-7.091081	1.539836	-0.592080	H	3.817851	-1.736229	-2.157963
H	-7.779061	-0.083173	-0.328080	H	2.567784	-2.996162	-1.993963
H	-6.855071	0.715839	0.967920	H	2.212864	-1.504143	-2.900963

Table S5 *continued*

PP-II conformer				α_L conformer			
H	-7.257907	-0.032979	-1.032012	H	-2.282900	-2.744957	-2.903963
C	-6.385903	-0.676973	-0.916012	C	-3.020902	-2.573969	-2.116963
H	-6.014901	-0.932971	-1.915012	H	-3.280886	-3.548973	-1.691963
H	-6.673897	-1.602975	-0.409012	H	-3.920910	-2.131984	-2.550963
C	-5.305908	0.087034	-0.167012	C	-2.389916	-1.718959	-1.032963
O	-5.208916	1.305034	-0.214012	O	-1.222914	-1.876940	-0.678963
N	-4.457903	-0.696961	0.586988	N	-3.192932	-0.746972	-0.496963
H	-4.403897	-1.670961	0.313988	H	-4.172932	-0.786988	-0.738963
C	-3.196906	-0.142953	1.052988	C	-2.869943	-0.066967	0.769037
H	-3.400913	0.890046	1.348988	H	-3.598957	0.748021	0.861037
C	-2.653901	-0.948949	2.241988	C	-2.976928	-0.986968	1.986037
H	-2.516894	-1.997948	1.958988	H	-2.267915	-1.811957	1.899037
H	-1.679904	-0.566943	2.557988	H	-2.738937	-0.433965	2.896037
H	-3.350902	-0.901954	3.081988	H	-3.990922	-1.388985	2.067037
C	-2.156906	-0.150946	-0.083012	C	-1.477954	0.601056	0.693037
O	-2.157901	-1.018946	-0.949012	O	-0.663953	0.497069	1.603037
N	-1.226913	0.848060	-0.024012	N	-1.249966	1.329060	-0.432963
H	-1.179916	1.405060	0.818988	H	-2.025969	1.480047	-1.059963
C	0.022088	0.740068	-0.749012	C	-0.054980	2.154079	-0.617963
H	-0.216909	0.275066	-1.711012	H	-0.096986	2.515079	-1.651963
C	0.618079	2.123072	-1.014012	C	-0.033000	3.372080	0.301037
H	1.490080	2.017078	-1.676012	H	-0.049994	3.041079	1.346037
H	-0.139925	2.734067	-1.525012	H	0.902992	3.915095	0.131037
O	0.996075	2.677074	0.238988	O	-1.181012	4.154061	-0.035963
H	1.399070	3.539077	0.078988	H	-1.186025	4.927061	0.541037
C	1.020094	-0.168926	-0.001012	C	1.244034	1.325101	-0.474963
O	0.994095	-0.311926	1.212988	O	2.223026	1.781117	0.100037
N	1.896098	-0.840920	-0.820012	N	1.242053	0.149101	-1.166963
H	1.995096	-0.465919	-1.756012	H	0.337059	-0.238914	-1.402963
C	3.144101	-1.347912	-0.267012	C	2.376068	-0.785881	-1.144963
H	2.904104	-1.738913	0.725988	H	2.014083	-1.680887	-1.664963
C	3.714109	-2.459908	-1.157012	C	3.595059	-0.234861	-1.883963
H	3.954106	-2.068907	-2.151012	H	3.957045	0.668145	-1.390963
H	4.633111	-2.867902	-0.727012	H	4.398071	-0.973848	-1.872963
H	2.986114	-3.266913	-1.264012	H	3.329056	-0.001865	-2.919963
C	4.155094	-0.186905	-0.149012	C	2.755076	-1.250875	0.288037
O	4.166088	0.725095	-0.971012	O	3.925078	-1.360856	0.633037
N	5.056095	-0.303899	0.863988	N	1.698082	-1.640892	1.054037
H	4.892099	-1.009900	1.564988	H	0.766078	-1.394907	0.747037
C	6.085088	0.692107	1.112988	C	1.861088	-2.006889	2.448037
H	5.853084	1.300106	1.994988	H	1.423076	-1.248896	3.107037
H	7.058091	0.214114	1.258988	H	1.387104	-2.972897	2.656037
H	6.129084	1.343108	0.239988	H	2.930090	-2.083872	2.648037

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Table S5 *continued*

β conformer			
H	-6.492977	1.986048	-0.190944
C	-6.486963	0.912048	-0.389944
H	-6.455961	0.747049	-1.469944
H	-7.420957	0.502036	0.005056
C	-5.324954	0.284064	0.363056
O	-5.196956	0.406066	1.576056
N	-4.451945	-0.437924	-0.405944
H	-4.537945	-0.432925	-1.412944
C	-3.252936	-1.060908	0.141056
H	-3.256940	-0.809908	1.205056
C	-3.260916	-2.580908	-0.050944
H	-3.251912	-2.826908	-1.115944
H	-2.375910	-3.032896	0.408056
H	-4.151910	-3.011920	0.412056
C	-2.043945	-0.438892	-0.576944
O	-1.881943	-0.598890	-1.782944
N	-1.227955	0.329119	0.198056
H	-1.360955	0.347117	1.201056
C	0.003037	0.926136	-0.299944
H	0.083041	0.650137	-1.353944
C	-0.032984	2.449135	-0.165944
H	-0.868989	2.841124	-0.762944
H	-0.206987	2.701133	0.889056
O	1.226010	2.930152	-0.617944
H	1.294997	3.864153	-0.382944
C	1.162045	0.355151	0.535056
O	1.209042	0.568152	1.745056
N	2.032055	-0.447837	-0.127944
H	1.997056	-0.500837	-1.136944
C	3.190064	-1.061821	0.520056
H	3.152059	-0.729822	1.561056
C	3.131084	-2.589822	0.443056
H	3.178089	-2.913821	-0.598944
H	3.979090	-3.033810	0.975056
H	2.205089	-2.955834	0.895056
C	4.447057	-0.539804	-0.195944
O	4.663061	-0.835801	-1.367944
N	5.256046	0.262207	0.547056
H	4.954042	0.516203	1.476056
C	6.448037	0.890223	0.002056
H	6.321023	1.974221	-0.094944
H	7.318040	0.690235	0.636056
H	6.616043	0.465225	-0.987944

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