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Supporting Information

Determination of accurate ^{1}H positions and intermolecular hydrogen bond distances of alanine tripeptide β-sheet structures by high resolution ^{1}H solid state NMR with ^{1}H chemical shift calculation by GIPAW method

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Experimental Methods

Alanine trimer, A_3, was purchased from Bachem AG (Bubendorf, Switzerland). AP and P A_3 were prepared by the method reported previously.[1]

All of solids state NMR experiments were performed using JEOL JNM-ECA920 in IMS equipped with ^{1}H-X double resonance ultra high speed MAS probe. The sample spinning speed was actively stabilized by a pneumatic solenoid valve so that the spinning fluctuations were less than ±10 Hz. The temperature of the samples increases due to friction effect of the fast MAS[2] and is estimated 333K at 70kHz MAS by $Pb(NO_3)_2$ temperature calibration.[3] The ^{1}H rf field strength for the excitation π/2 pulse (1.29 μs) was 200kHz. The ^{1}H chemical shift was referenced to the peak of silicon rubber and set to 0.12 ppm from

TMS.

For ^{1}H DQMAS, Dipolar Homonuclear Homogeneous Hamiltonian double-quantum/single-quantum (DQ–SQ) correlation measurement (DH_3) was employed. [4] This sequence consists of five pulses, which is identical to the refocused INADEQUATE sequence, and suffers less from the problems of B1 inhomogeneity and frequency offset. The 2τ delay was optimized, and 0.3 ms giving maximum S/N was used. The DQMAS spectra required 32scans each period in DQ domain, and a recycle delay was set to 2s.

The generalized gradient approximation (GGA) for the exchange correlation energy using the Perdew, Bruke and Ernzerhof (PBE) functional and ultrasoft pseudopotentials was used for geometry optimization and the gauge-including projector augmented wave (GIPAW) chemical shift calculations. The geometry optimization was performed starting with the X-ray diffraction crystal structure of AP[5] and P[6] A_3, and applied only for protons under the periodic boundary condition. All calculations were carried out by the CASTEP program.[7]

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Details of DQMAS peak assignment for P-A_3

The peak of NH_3 is assigned to 9.0 ppm from the diagonal peak. The area ratio of NH_3 and NH protons, 3:2, in the 1D spectrum corresponds with the assignment. The cross peaks between the NH_3 and H_α are apparent at δ_{DQ} = 9.0 + 4.9 = 13.9 ppm with strong intensity and δ_{DQ} = 9.0 + 4.4 = 13.4 ppm with weak intensity. The former is correlation with 1-H_α in a same residue (8 in Fig.2e) (2.60Å for A, and 2.63Å for B in average), and the latter is inter-molecular head-to-tail correlation with 3-H_α. (9 in Fig.2e) (3.22Å for NH_3(A)-H_α(B), 3.46Å for NH_3(B)-H_α(A) in average). Consequently, 2H_α should be the remained peak at 5.5ppm. 2- and 3-NH are assigned by the similar manner with AP except that inter-molecular proximities of same residues between A and B molecules are observable. The assignments are consequently resulted in 2-H_N = 7.5 ppm, and 3-H_N = 7.2 and 7.4 ppm.

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Table S1. Experimental and Calculated (GIPAW) ^{1}H Isotropic Chemical Shifts (ppm) for AP and P A_3 (single quantum).

		Expt.	Calc. X-ray[a]	Calc. Opt[a]
AP A_3	NH_3	9.1	9.35(A), 7.52(B)	9.47(A), 9.41(B)
	$2H_N$	8.6	5.38(A), 6.36(B)	9.14(A), 9.43(B)
	$3H_N$	8.3	7.22(A), 7.85(B)	8.73(A), 8.40(B)
	1Hα	4.5, 4.1	6.72(A), 6.03(B)	4.52(A), 4.05(B)
	2Hα	4.7	5.16(A), 6.61(B)	4.86(A), 4.76(B)
	3Hα	3.9, 3.8	5.24(A), 6.11(B)	3.85(A), 3.72(B)
P A_3	NH_3	9.0	7.18(A), 7.13(B)	9.31(A), 9.15(B)
	$2H_N$	7.5	6.87(A), 6.87(B)	7.50(A), 7.61(B)
	$3H_N$	7.4, 7.2	6.73(A), 6.49(B)	7.50(A), 7.26(B)
	1Hα	4.9	4.95(A), 4.97(B)	4.75(A), 4.84(B)
	2Hα	5.5	5.80(A), 5.58(B)	5.52(B), 5.44(B)
	3Hα	4.4	4.50(A), 4.57(B)	4.37(A), 4.55(B)

[a] The calculated ^{1}H chemical shifts are referenced to the average of three chemical shifts of CH_3, and set to experimentally obtained values, 1.30 ppm for AP and 1.36 ppm P A_3.

Table S2. Experimental and Calculated (GIPAW) ^{13}C Isotropic Chemical Shifts (ppm) for AP and P A_3 (single quantum).

		Expt.[a]	Calc. *X-ray*[a]	Calc. *Opt.*[a]
AP A_3	1C=O	170.7(A), 170.1(B)	172.5(A), 173.0(B)	170.1(A), 170.5(B)
	2C=O	171.1(A), 170.3(B)	172.3(A), 175.9(B)	168.4(A), 171.5(B)
	3C=O	178.7(B), 178.5(B)	182.3(A), 181.9(B)	179.5(A), 178.6(B)
	1Cα	47.9(A), 49.3(B)	44.1(A), 44.7(B)	49.1(A), 48.5(B)
	2Cα	50.6(A), 50.0(B)	44.6(A), 47.9(B)	50.7(A), 52.7(B)
	3Cα	53.8(A), 50.4(B)	46.6(A), 52.2(B)	51.5(A), 55.7(B)
	1C_β	19.0(A), 19.7(B)	-0.1(A), -2.2(B)	18.8(A), 17.9(B)
	2C_β	20.6(A), 20.1(B)	-1.9(A), 1.7(B)	18.4(A), 18.4(B)
	3C_β	19.9(A), 19.2(B)	6,7(A), 7.7(B)	17.6(A), 18.6(B)
P A_3	1C=O	170.1(A), 171.3(B)	169.3(A), 173.1(B)	168.9(A), 173.1(B)
	2C=O	171.2(A), 170.8(B)	168.6(A), 173.3(B)	168.5(A), 173.2(B)
	3C=O	178.8(A), 179.4(B)	178.6(A), 179.8(B)	180.1(A), 182.4(B)
	1Cα	49.1(A), 50.3(B)	54.3(A), 54.3(B)	54.1(A), 54.2(B)
	2Cα	47.9(A), 49.8(B)	53.0(A), 55.7(B)	52.5(B), 54.2(B)
	3Cα	49.8(A), 52.8(B)	49.6(A), 55.7(B)	49.5(A), 55.2(B)
	1C_β	19.2(A), 16.2(B)	22.9(A), 18.5(B)	20.1(A), 16.3(B)
	2C_β	21.5(A), 21.0(B)	24.1(A), 22.8(B)	21.0(A), 20.0(B)
	3C_β	22.3(A), 20.4(B)	26.1(A), 22.9(B)	22.6(A), 20.6(B)

[a] Experimental data of Asakura et al.[1] obtained from ^{13}C CP/MAS spectra.

[b] Calculated chemical shifts are set to minimize RMSD between the calculated and the observed data. The RMSD values are 9.20 for *X-ray*. and 1.95 for *Opt* in AP, and 2.21 for *X-ray* and 2.27 for *Opt* in P.

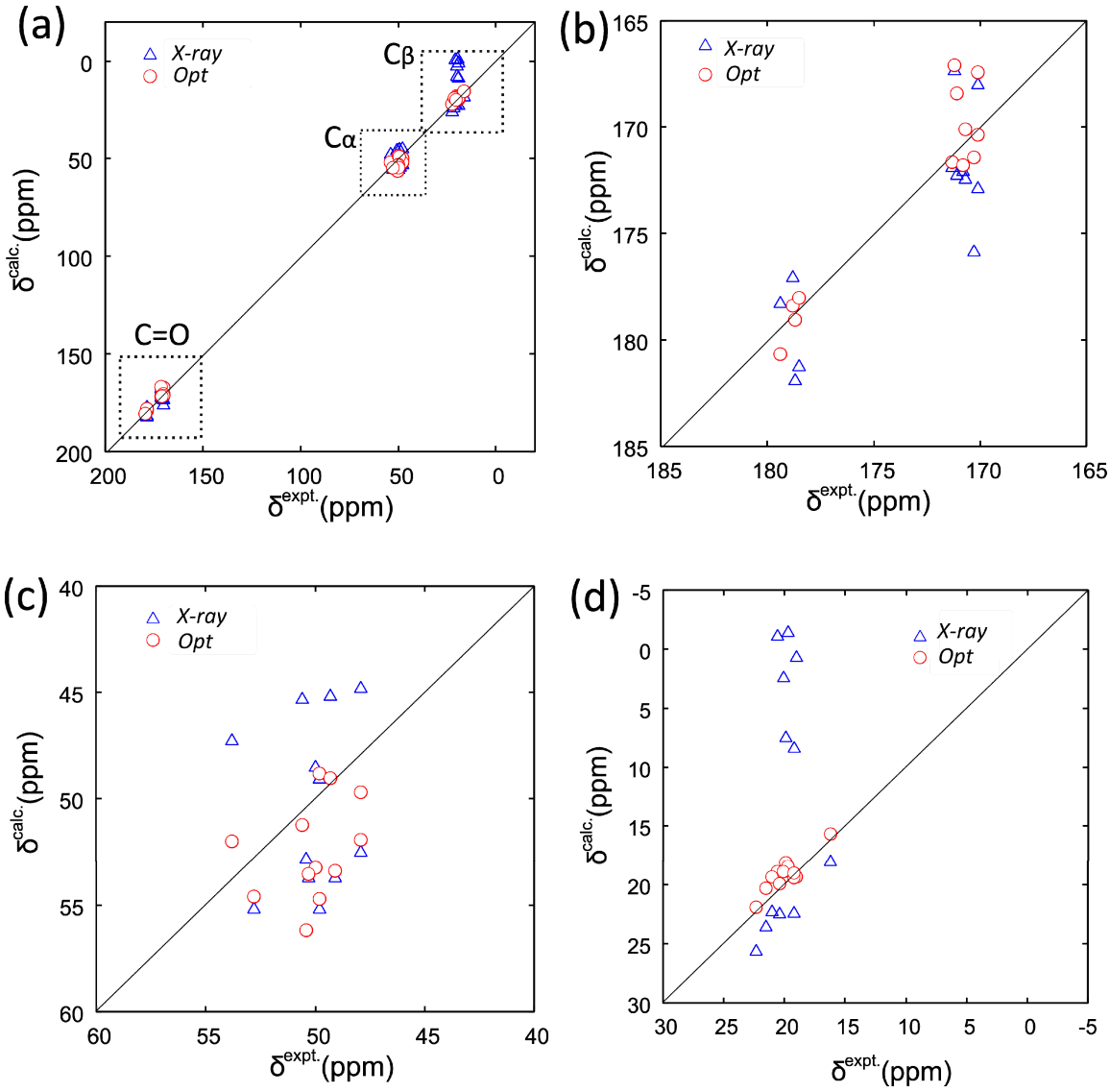

Figure S1. (a) Comparison of the observed ($\delta^{expt.}$) and calculated ($\delta^{calc.}$) ^{13}C chemical shits of A_3 for the whole region, (b) the carbonyl region, (c) the C_α region, and (d) the C_β region.

Table S3. Experimental and Calculated (GIPAW) ^{15}N Isotropic Chemical Shifts (ppm) for AP and P A_3.

		Expt.[a]	Calc. *X-ray*[b]	Calc. *Opt*[b]
AP A_3	1N (NH_3)	19.6(A), 16.5(B)	14.3(A), 1.9(B)	18.1(A), 14.0(B)
	2N	100.0	104.1(A), 102.5(B)	102.0(A), 100.6 (B)
	3N	109.3(A), 105.5(B)	115.4(A), 114.2(B)	109.4(A), 107.0(B)
P A_3	1N(NH_3)	19.4	16.5(A), 16.0(B)	19.6(A), 19.4(B)
	2N	95.1(A), 98.0(B)	99.0(A), 102.5(B)	97.3(A), 101.4(B)
	3N	101.8	108.1(A), 107.3(B)	106.3(A), 105.4(B)

[a] Experimental data of Suzuki et al.[8] obtained from ^{15}N CP/MAS spectra.

[b] Calculated chemical shifts are set to minimize RMSD between the calculated and the observed data. The RMSD values are 2.30 for *X-ray* and 2.02 for *Opt*. in AP, and 3.94 for *X-ray* and 1.72 for *Opt* in P.

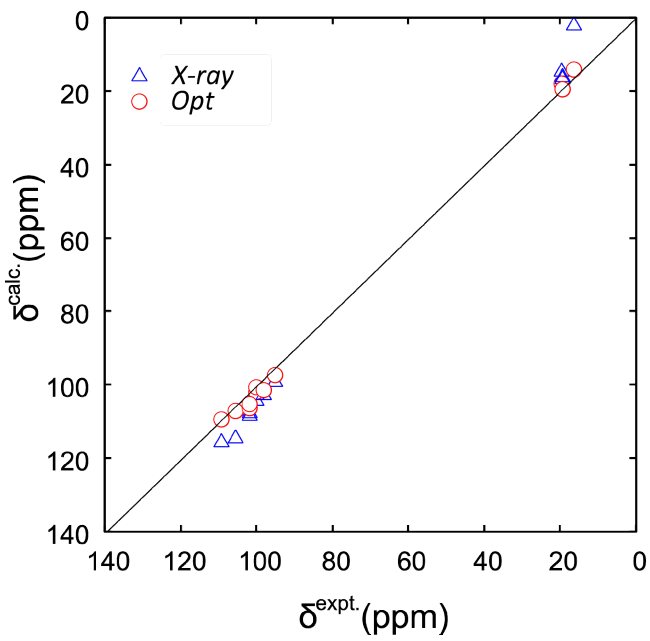

Figure S2. (a) Comparison of the observed ($\delta^{expt.}$) and calculated ($\delta^{calc.}$) ^{15}N chemical shits of A_3.

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Table S4. Calculated geometric hydrogen-bond correlations of AP and P A_3 (*Opt*).

		dOH(Å)	dNH(Å)
AP A_3	$2H_N$	1.94(A), 1.92(B)	1.04(A), 1.04(B)
	$3H_N$	1.99(A), 2.08(B)	1.03(A), 1.03(B)
P A_3	$2H_N$	2.27(A), 2.46(B)	1.03(A), 1.03(B)
	$3H_N$	2.28(A), 2.39(B)	1.03(A), 1.03(B)

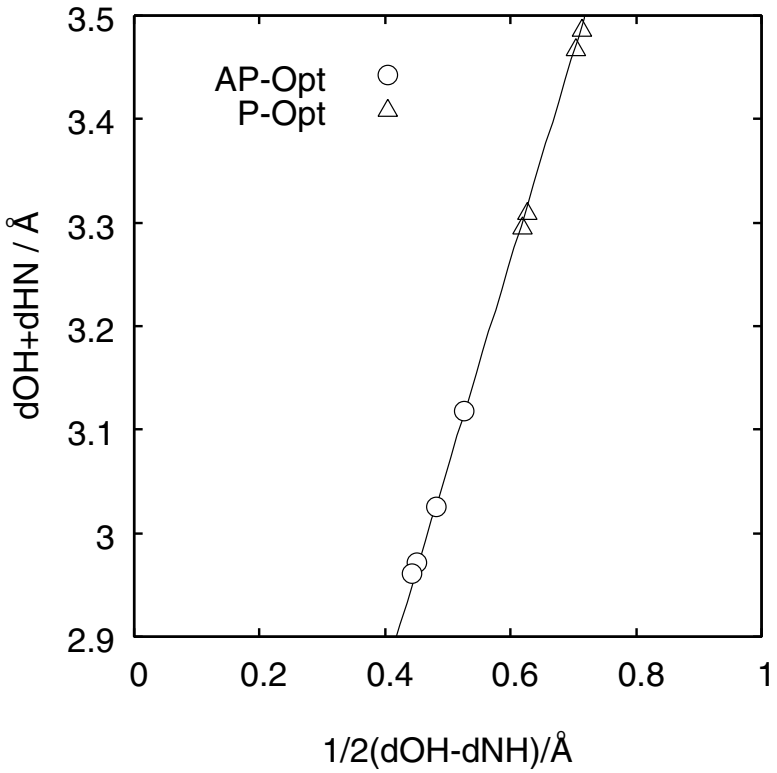

Figure S3. Geometric OHN intermolecular hydrogen bond correlations. The values *d*OH and *d*NH are *Opt* geometry listed in Table S2. 1/2(*d*OH-*d*NH) represents the distance of H from the hydrogen bond center and *d*OH+*d*NH the distance between the heavy atom O and N. Note that the correlation is not dependent on the H-bond angle.

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