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Supporting Information

Crystallographic and Dynamic Aspects of Solid-State NMR Calibration Compounds: Towards ab Initio NMR Crystallography

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Supporting Information for "Crystallographic and dynamics aspects of solid-state NMR calibration compounds: towards *ab initio* NMR crystallography"

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Compound	Method	Carbon	Exp. CS [ppm]	Cal. CS [ppm]	Deviation [ppm]
α-glycine	MD	CO	176.5	169.1	-7.4
		CH_2	43.7	46.9	3.2
γ-glycine	MD	CO	173.4	163.6	-9.8
		CH_2	41.4	52.5	11.1
adamantane	MD	CH	29.5	31.4	2.0
		CH_2	38.5	40.0	1.4
hexamethylbenzene	MD	CH	132.0	130.0	-2.0
		CH_3	17.2	16.7	-0.5
3-methylglutaric acid	MD	COOH(1)	180.7	179.5	-1.2
		COOH(2)	181.6	180.3	-1.3
		CH_2(1)	38.3	40.5	2.2
		CH_2(2)	39.5	43.5	3.9
		CH	25.2	24.7	-0.6
		CH_3	18.8	17.9	-1.0
MAD [ppm]	3.4				
RMSD [ppm]	4.8				
Ref. shielding [ppm]	169.5				

Table S1. Calculated and experimental chemical shifts of the five calibration phases when MD with the COMPASS force field was employed for the two polymorphs of glycine, which gave large distortions during the energy minimizations (see Figure S1). CS: chemical shift, MAD: mean-absolute deviation, RMSD: root-mean-square deviation.

Compound	Method	Carbon	Exp. CS [ppm]	Cal. CS [ppm]	Deviation [ppm]
α-glycine	DFT-D	CO	176.5	179.2	2.7
		CH_2	43.7	41.7	-2.0
γ-glycine	DFT-D	CO	173.4	176.3	2.9
		CH_2	41.4	40.0	-1.4
adamantane	MD	CH	29.5	30.8	1.3
		CH_2	38.5	39.3	0.8
hexamethylbenzene	MD	CH	132.0	129.3	-2.7
		CH_3	17.2	16.0	-1.2
3-methylglutaric acid	DFT-D	COOH(1)	180.7	186.3	5.6
		COOH(2)	181.6	186.5	4.8
		CH_2(1)	38.3	36.7	-1.7
		CH_2(2)	39.5	36.8	-2.7
		CH	25.2	22.7	-2.6
		CH_3	18.8	14.9	-3.9
MAD [ppm]	2.6				
RMSD [ppm]	2.9				
Ref. Shielding [ppm]	168.8				

Table S2. Calculated and experimental chemical shifts when using the DFT-D energy minimized 3-methylglutaric acid to fit with the other four calibration phases. CS: chemical shift, MAD: mean-absolute deviation, RMSD: root-mean-square deviation.

		a [Å]	*b* [Å]	*c* [Å]	α [°]	β [°]	γ [°]	Volume [Å^3]
Adamantane Space group: $Fm\bar{3}m$ Z = 4	Experiment	9.445	9.445	9.445	90	90	90	842.570
	1 × 1 × 1 MD	9.583	9.583	9.583	90	90	90	879.906
	Δ [%]	1.461	1.461	1.461				4.431
Hexamethylbenzene Space group: $P\bar{1}$ Z = 1	Experiment	5.300	6.272	8.098	103.837	99.451	99.584	251.806
	2 × 2 × 2 MD	5.262 × 2	6.524 × 2	8.066 × 2	105.524	99.250	96.806	259.514
	Δ [%]	-0.717	4.018	-0.395	1.625	-0.202	-2.790	3.061
α-Glycine Space group: $P2_1/n$ Z = 4	Experiment	5.010	11.952	5.459	90	111.781	90	309.005
	1 × 1 × 1 MD	4.947	15.220	5.300	90	119.811	90	346.248
	Δ [%]	-1.257	27.343	-2.913		7.184		12.053
γ-Glycine Space group: $P3_1$ Z = 3	Experiment	7.038	7.038	5.481	90	90	120	235.153
	1 × 1 × 1 MD	8.460	8.437	4.250	88.041	94.131	120.101	261.784
	Δ [%]	20.205	19.878	-22.459	-2.177	4.590	0.084	11.325
3-Methylglutaric acid Space group: $P2_1/c$ Z = 4	Experiment (293 K)	13.909	5.367	10.307	90	110.554	90	720.4
	1 × 1 × 1 MD	13.962	5.309	10.456	90	110.754	90	724.751
	Δ [%]	0.381	-1.081	1.446		0.181		0.605

Table S3. Experimental lattice parameters and averaged lattice parameters from the MD simulations with the COMPASS force field.

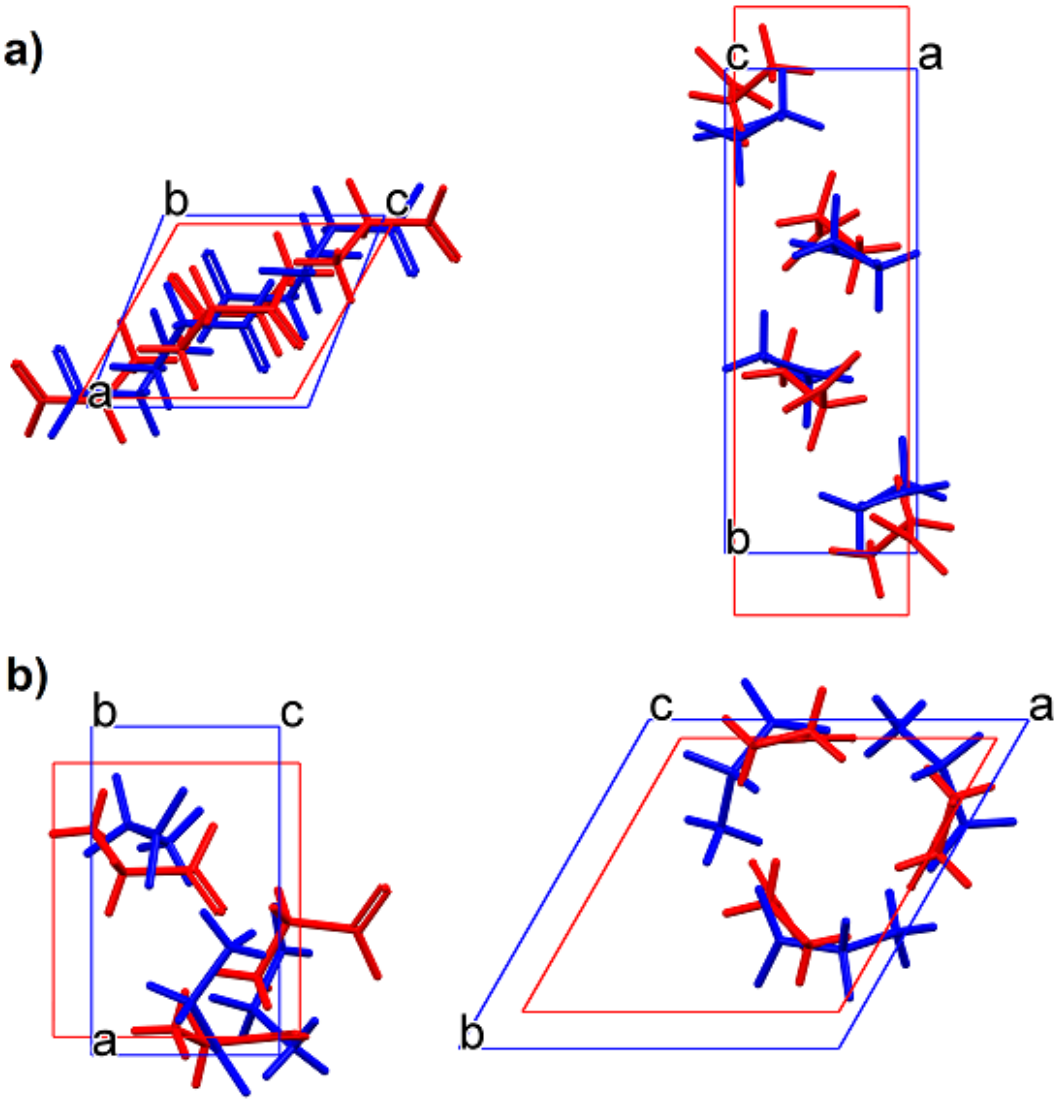

Figure S1. Overlays of the COMPASS force field energy minimized (blue) and the experimental (red) structures for a) the α-polymorph of glycine and b) the γ-polymorph of glycine. Large distortions can be identified in the energy minimizations.

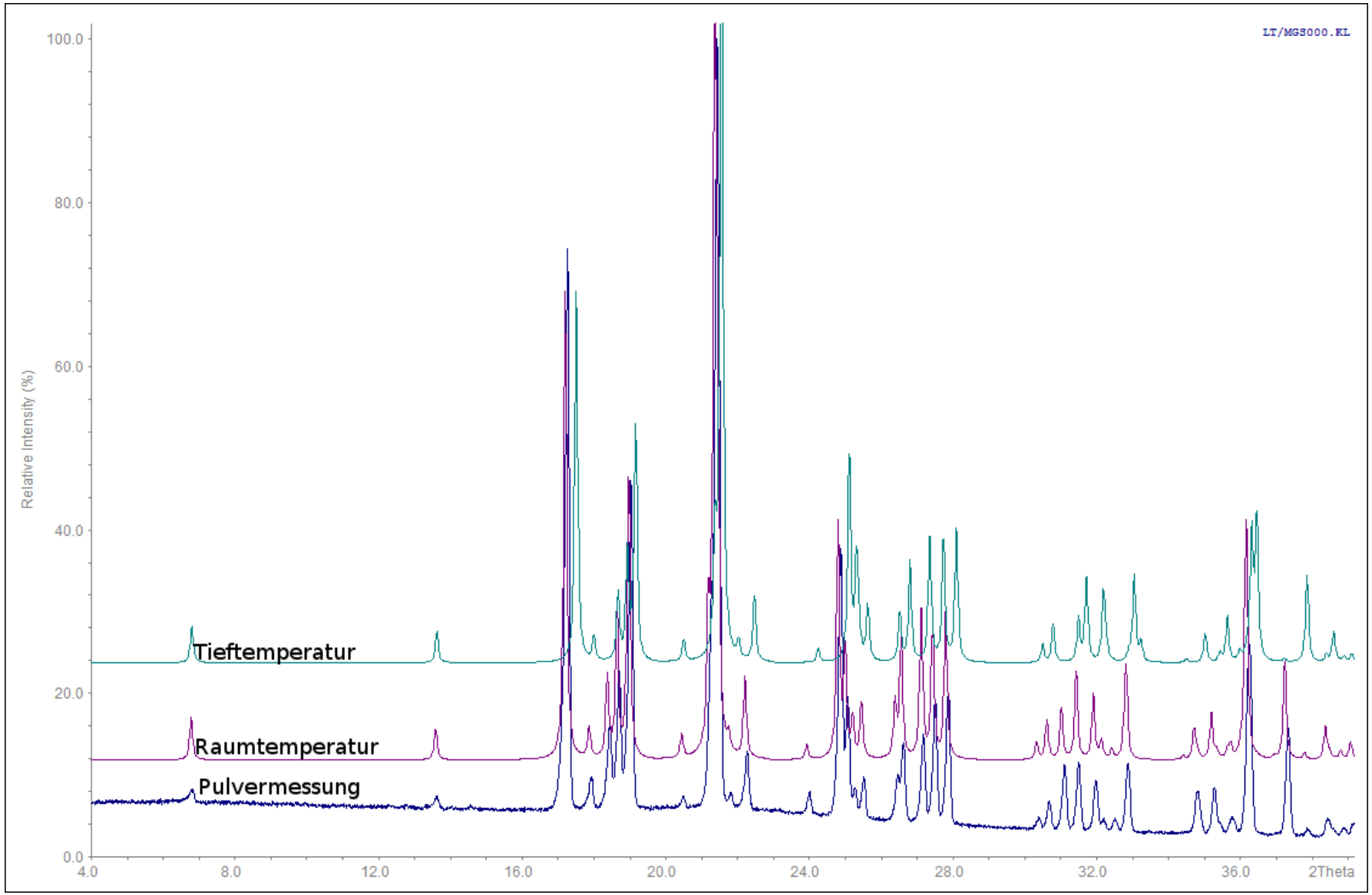

Figure S2. The X-ray powder diffraction patterns of 3-methylglutaric acid. From the top to the bottom: (1) Calculated pattern of the low-temperature structure (Tieftemperatur); (2) Calculated pattern of the room-temperature structure (Raumtemperatur) and (3) the experimentally measured pattern at room-temperature (Pulvermessung).

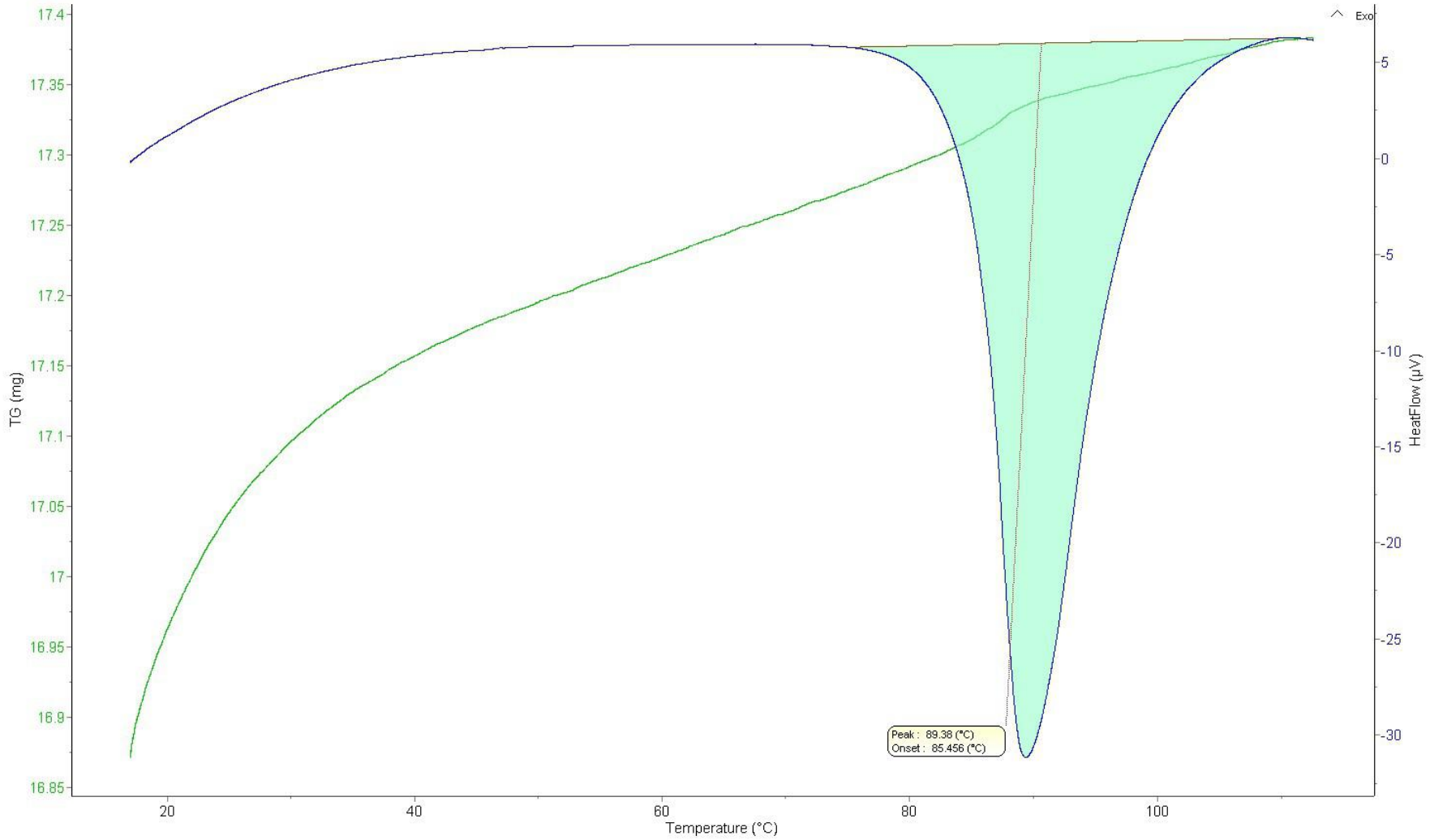

Figure S3. The differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) pattern of the purchased sample of 3-methylglutaric acid.