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Supporting Information

Solid-State ^{17}O NMR Reveals Hydrogen-Bonding Energetics: Not All Low-Barrier Hydrogen Bonds Are Strong

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Supporting Information

Experimental section

Synthesis: [1,2-$^{17}O_2$]NA was prepared in the following fashion. A mixture of nicotinic acid (663 mg, 5.39 mmol), ^{17}O-enriched water (600 μL, 40% ^{17}O, purchased from CortecNet) in 4 M HCl 1,4-dioxane (5 mL) was heated in a closed pressure-tube at 80 °C (oil-bath) for 1 h, and then at 110 °C overnight. Upon cooling the solution in an ice-bath, the solid material was collected, and then washed with cold water (1 mL), giving the HCl slat of the title compound (667 mg, 77.5%). This HCl-salt (403 mg, 2.52 mmol) was treated with a solution of MeONa (30% MeONa solution in MeOH, 432 mg) in EtOH (10 mL) in an oil-bath (80 °C) for 10 min. The mixture was evaporated to dryness (rotary evaporator). Cold water (1 mL) was added to the flask. The solid material was collected by filtration, washed with cold water (1 mL), and dried, giving the title compound as a white solid (160 mg, 52%): ^{17}O NMR (DMSO-d_6, 68 MHz), δ = 257 ppm. The ^{17}O enrichment level in the final product was determined to be 18%. [^{15}N]NA was prepared following a literature method.[1] [1-^{2}H]NA was prepared by repeated recrystallization of NA from methanol-d_4 (99.8% D).

Solid-state NMR: All solid-state NMR experiments, except for the ^{1}H fast MAS experiment, were performed at the National High Magnetic Field Laboratory on an ultrawide bore 21.1 T magnet using a Bruker Avance III console and a homebuilt 3.2 mm HX transmission line probe. 1D ^{15}N CP/MAS and 2D ^{1}H-^{15}N CP HETCOR spectra were acquired for [^{15}N]NA. Variable temperature ^{17}O MAS spectra were recorded for [1,2-$^{17}O_2$]NA at a spinning frequency of 20 kHz. The sample temperatures under the 20 kHz MAS condition were calibrated using the ^{207}Pb NMR signal from a solid sample of $Pb(NO_3)_2$. The 60-kHz MAS ^{1}H NMR spectrum was acquired at 21 T (900 MHz) at the National Ultrahigh Field NMR Facility for Solids (Ottawa, Canada). The ^{1}H chemical shift was referenced to TMS by setting the ^{1}H NMR signal of admantane to 1.8 ppm. All ^{15}N and ^{17}O chemical shifts were referenced to liquid NH_3 and H_2O, respectively.

X-ray diffraction: Diffraction data were collected for a single crystal of NA at 180 K on a Bruker SMART APEX II X-ray diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), operating at 50 kV and 30 mA over 2θ ranges of 5.40-52.00°.

Plane-wave DFT calculations: All quantum chemical and MD calculations were performed using the CASTEP code (version 2017)[2] together with BIOVIA's Materials Studio. For all calculations, the generalized gradient approximation with the Perdew-Burke-Ernzerhof exchange correlation functional was chosen. The adiabatic 1D HB potential mapping was obtained by changing the position of the H atom stepwise along the O···N HB direction and then optimizing the entire system for each step while keeping the positions of the O, H, and N atoms in question fixed. For the calculation of the COO rotational barrier energy the C-C-C-O torsional angle was varied in steps and constraint, while the geometry of the rest of the molecule was optimized using the BFGS algorithm, ultrasoft pseudopotentials, a cut-off energy of 340 eV and a 2×1×2 *k*-point grid. The MD calculation in CASTEP was performed in three steps: 1) fully optimize the geometry OH

and NH form of the molecule, 2) perform a MD runs on each molecule until thermal equilibrium is reached, and finally 3) perform the actual MD calculations and combine the results. For all three steps, OTFG ultrasoft pseudopotentials together with a cut-off energy of 489.8 eV and a 2×1×2 *k*-point grid was chosen. The integration time-step was set to 0.5 fs, and the canonical (NVT) ensemble held at a constant temperature of 370 K employing a Langevin thermostat was used. The MD run to thermal equilibrium lasted a total of 0.5 ps using a thermostat time constant of 0.1 ps. The total simulation time of the actual MD calculations was 2.5 ps, where a thermostat time constant of 0.5 ps was used, resulting in a mean temperature of 360 K with a standard deviation of 35 K. The complete MD runs took 6.5 days on a dual Intel Xeon six-core 2.93 GHz processor workstation.

Table S1. Relative energy per NA molecule as a function of the C-C-C-O torsion angle (rotation of the carboxylate group about the C-C bond) obtained from plane-wave DFT calculations using the CASTEP code.

Torsion Angle (º)	Relative energy (kcal mol^{-1})
8.336	0
38.336	2.02
68.336	7.59
83.336	11.04
88.336	11.85
93.336	12.40
98.336	12.55
103.336	12.17
108.336	11.74
113.336	11.15
128.336	9.62
158.336	6.92

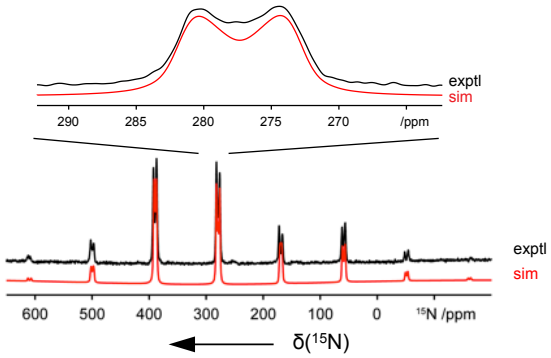

Figure S1. Experimental (black trace) and simulated (red trace) 1D ^{1}H-^{15}N dipolar recoupled CP/MAS spectrum of [^{15}N]NA recorded at 213 K. The spectrum was acquired at 10 kHz MAS with ^{1}H-^{15}N dipolar recoupling during t_2 using the R18$^{7}_{1}$ sequence[3] with a ^{1}H recoupling B_1 field of 90 kHz, recycle delay of 4 s; 340 transients were averaged. From the simulation, the value of the ^{1}H-^{15}N dipolar coupling constant was determined to be 2400 Hz, which corresponds to an averaged ^{1}H-^{15}N distance of 1.72 Å. From the simulation, the ^{15}N chemical shift tensor components were also obtained; see Table 1 given in the main text.

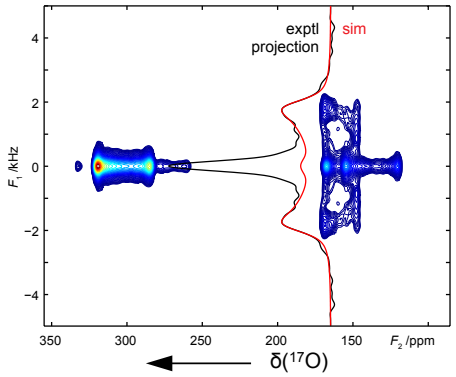

Figure S2. Experimental 2D ^{17}O{^{1}H} dipolar recoupled DIPSHIFT spectrum of [1,2-$^{17}O_2$]NA collected at 213 K. A spin-echo was acquired at 20 kHz MAS with ^{1}H-^{17}O dipolar recoupling during the inter-pulse delay of 3 ms using the R18$^{5}_{2}$ sequence[4] with a ^{1}H recoupling B_1 field of 45 kHz, 90 kHz ^{1}H decoupling during full-echo acquisition, and a ^{17}O selective π/2-pulse of 2 μs with a B_1 field of 42 kHz. The spectrum was acquired with a spectral width of 10 kHz and 30 real points in t_1, recycle delay of 0.2 s and 12288 transients per t_1 point resulting in a total experimental time of 20.5 h. From the simulation, the value of the ^{1}H-^{17}O dipolar coupling constant was determined to be 12700 Hz, which corresponds to an averaged ^{1}H-^{17}O distance of 1.09 Å

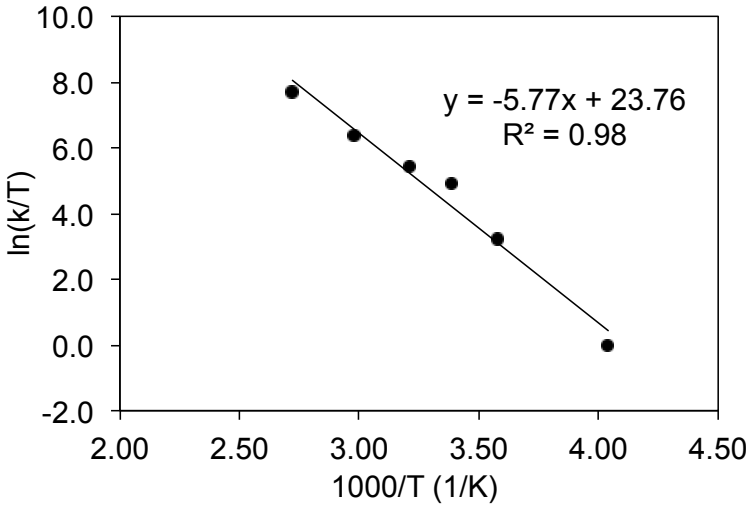

Figure S3. Eyring plot for the carboxylate flip motion in NA.

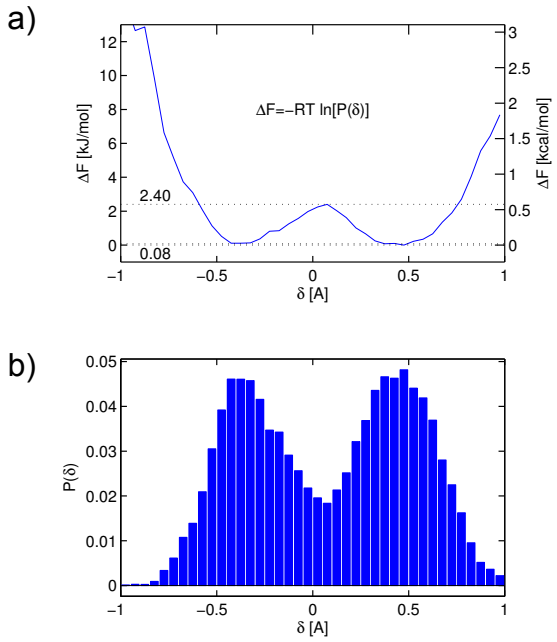

Figure S4. a) 1D potential energy curve and b) proton probability distribution histogram from plane-wave DFT MD simulations for NA. δ is defined as $r_{HN} - r_{OH}$.

References

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