Electronic Supplementary information

Solid-state NMR and DFT predictions of differences in COOH hydrogen bonding in odd and even numbered *n*-alkyl fatty acids.

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Assigning ^{13}C chemical shifts

Assignments of ^{13}C chemical shifts for lauric acids (phase C) were made by first acquiring a series of $^{1}H/^{13}C$ heteronuclear correlation (HETCOR) spectra. A total of three spectra were acquired employing cross-polarization times of 100 μs, 200 μs and 300 μs. These spectra identified the $^{1}H \rightarrow {}^{13}C$ correlations shown in Figure 1 and provided assignments for C1 – C4, C11 and C12.

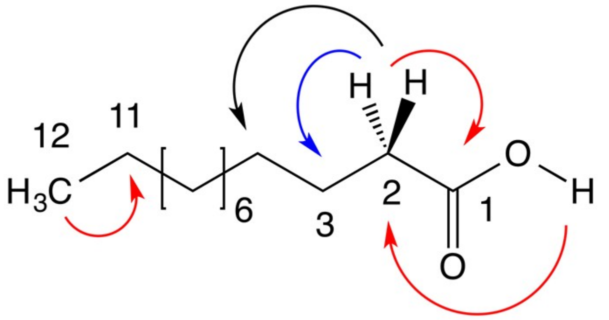

Figure 1. The $^{1}H \rightarrow {}^{13}C$ correlations observed in a HETCOR analysis of lauric acid, phase C. The red, blue and black lines show correlations best observed at contact times of 100μs, 200 μs and 300 μs. One-bond $^{1}H \rightarrow {}^{13}C$ correlations were also observed in all spectra but are not included here.

A second approach was employed to assign C5 and C10 that involved calculating ^{13}C chemical shift tensors for lauric acid using the single crystal x-ray structure and comparing these data to experimental tensors. For this analysis, all atoms of lauric acids was refined using the planewave DFT code CASTEP and then NMR tensors were computed using the GIPAW method. Both computations were conducted at the PBE/ultrafine level of theory. The best fit between theory and experiment provided assignments for C5 and C10.

Carbons 6–9 were nearly degenerate in both the isotropic shifts and in the tensor principal values and thus could not be assigned by either of the methods described above. The shift assignments given in the text for C6–C9 are therefore interchangeable.

Energy versus O–H separation

Energies were computed for the lauric acid to evaluate the influence of disorder on hydrogen bond strength. All computations were performed using CASTEP to include lattice effects and employed the PBE functional with the ultrafine pseudopotential. Structures evaluated began with an O–H bond length of 1.00 Å and a O=C-Cα-Cβ dihedral angle of 180° (i.e. the *trans* conformation) and then increased the bond length in steps ranging in size from 0.04 to 0.1 Å until a bond length of 1.70 Å was achieved. This final structure corresponds to the *cis* structure with a O=C-Cα-Cβ dihedral angle of 0°.

Table 1. Energy vs. O–H bond length for lauric acid phase C

O–H separation (Å)	Energy[a] (kJ mol^{-1})
1.00	4.8
1.04 (*trans*)	0.0
1.10	9.6
1.20	32.8
1.30	36.7
1.40	26.1
1.50	14.5
1.60 (*cis*)	9.6
1.70	13.5

[a] All energies are given relative to the lowest energy (r = 1.04 Å), which is arbitrarily given a value of zero.

The Boltzmann populations of the two minima at O–H separations of 1.04 Å and 1.60 Å are 98.0% and 2.0% , respectively.

Identifying best-fit O–H hydrogen positions using CASTEP

In all structural comparisons, a butyric acid dimer model hydrogen bonded in an $R_2^2(8)$ arrangement was employed to evaluate the most favorable O–H distances. In order to verify that this model gives comparable results to computational methods that include lattice effects, a study was performed in which the crystal structure for lauric acid phase C was evaluated in an environment that includes lattice effects at the PBE/ultrafine level of theory. A series of 8 structures were prepared that were identical except that the O–H separation varied from 1.0 to 1.7 Å in steps of 0.1 Å. Each structure was optimized using CASTEP while holding the O–H distance unchanged and NMR shift tensor were computed using GIPAW (PBE/ultrafine) for the relaxed structure. The best-fit O–H separations were found at 1.1 Å and 1.4 Å. These values agree favorably with the O–H separations of 1.16 and 1.46 Å obtained using the butyric acid dimer. The NMR agreement versus O–H separation is illustrated in Figure 2.

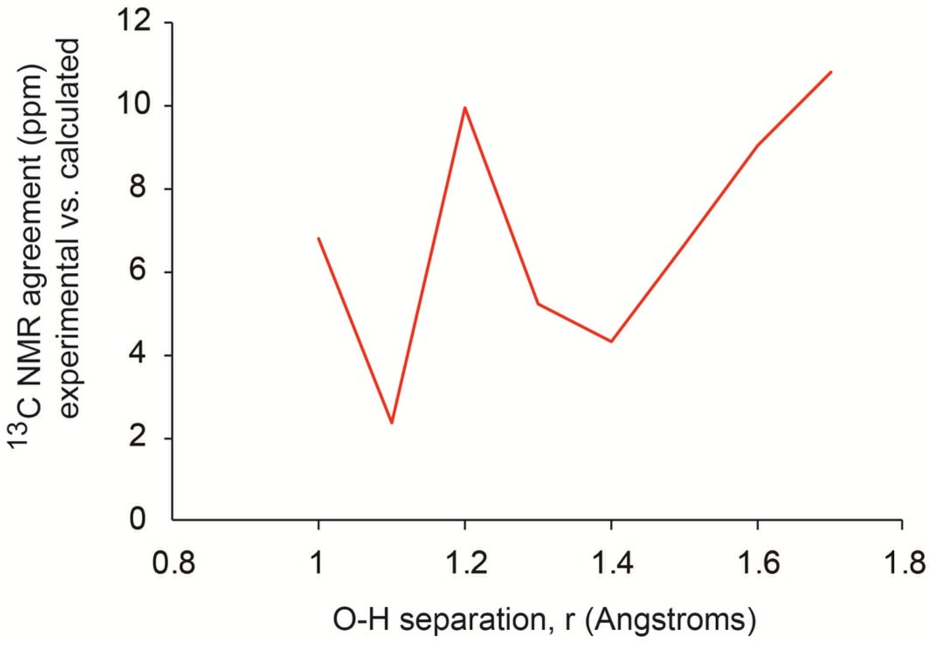

Figure 2. The agreement between experimental and computed ^{13}C principal values for the COOH in lauric acid versus O–H separation. Here, calculated ^{13}C shift tensors were computed using GIPAW utilizing the crystal structure of lauric acid phase C to include lattice effects. The best-fit O–H distances of 1.1 Å and 1.4 Å compare favorably with the values of 1.16 Å and 1.46 Å obtained when the butyric acid dimer was used as a model structure.