SUPPORTING INFORMATION

Can Non-polar Hydrogen Atoms Accept Hydrogen Bonds?

Lixu Yang, Thomas A. Hubbard and Scott L. Cockroft*

EaStCHEM School of Chemistry, University of Edinburgh, King's Buildings, West Mains Road, Edinburgh, EH9 3JJ, UK

E-mail: scott.cockroft@ed.ac.uk

Contents

- -NMR Methods and Data
- -Computational Methods and Data

NMR Methods and Data

All compounds were purchased from *Sigma-Aldrich*, or *Fluoro Chem*. Solvents were dried over molecular sieves. ¹H NMR spectra were recorded on either 400 or 500 MHz Bruker Avance III spectrometer. ¹⁹F NMR spectra were recorded on a 400 MHz Bruker Avance III spectrometer. ¹H NMR chemical shifts are reported in parts per million (δ) relative to trimethylsilane ($\delta = 0$) as an internal reference. Where non-deuterated solvents were used, ¹⁹F chemical shifts were referenced against 20 mM trifluoroacetic acid in D₂O ($\delta = -76.55$), which was contained within a sealed capillary tube. Guest solutions were prepared using host stock solution, such that the host concentration was kept constant during titration experiments. Data were fitted to a 1:1 binding isotherm using an *Excel* spreadsheet which was kindly provided by Prof Christopher A. Hunter (University of Sheffield).

Reported errors are twice the standard error ($\approx 95\%$ confidence interval).

Titration number	<i>K</i> ∕M ^{−1}	% bound	<mark>δ_F free</mark> / ppm	<mark>δ_F bound</mark> ∕ ppm	Δδ _{F free→bound} / ppm	Fitting error / %	[PFTB] / mM	Range [THS] / mM
1	0.689	58	-74.805	-74.139	+0.666	3.9	1.004	0 - 1993
2	0.631	31	-74.805	-74.163	+0.643	1.8	5.738	0 - 724
3	0.943	57	-74.866	-74.339	+0.527	1.9	5.379	0 - 1404
mean	0.8 ± 0.3	-	-	-	+0.61 ±0.14	-	-	-

Table S1: Experimental 1:1 binding data for the titration of trihexylsilane (THS) against a constant concentration of perfluoro-*tert*-butanol (PFTB) in cyclohexane. Errors are twice the standard error.



Figure S1. Stack plot of the ¹⁹F-NMR titration depicted in Figure 5 showing the shift of the ¹⁹F signal in perfluoro-*tert*-butanol (relative to an internal standard contained within a capillary tube) on increasing the concentration of trihexylsilane in cyclohexane solution at 298 K.



Figure S2. Stack plot of the ¹⁹F-NMR titration of the control tetraethylsilane (which lacks an Si-H Hbond acceptor) showing the shift of the ¹⁹F signal in perfluoro-*tert*-butanol (relative to an internal standard contained within a capillary tube) on increasing the concentration of tetraethylsilane in cyclohexane solution at 298 K.

Computational Methods and Data

Minimised geometries and molecular surfaces were calculated using *Spartan '08* or *Spartan '14* using the methods stated. Electrostatic potentials are plotted on the 0.002 electrons/bohr³ density surface.



Figure S3. Calculated electrostatic potentials (B3LYP/LACVP) showing from left to right, tri-*n*-hexylsilane (the weakly electron-rich H atom bonded to the silicon centre appears in yellow, $\text{ESP} = -47 \text{ kJ mol}^{-1}$), cyclohexane, and finally, the very strong H-bond donor, perfluoro-*tert*-butanol. Electrostatic potentials are scaled from -100 kJ mol^{-1} (red) to $+100 \text{ kJ mol}^{-1}$. Green corresponds to 0 kJ mol⁻¹.

						ОН			SiH
Theory/	BSSE (CP) Energy / kJ	H H dist.	H H-Si angle	OH _{free} bond length	OH _{bound} bond length	^{free→bound} bond length change	SiH _{free} bond length	SiH _{bound} bond length	^{free→bound} bond length change
basis set	mol ⁻¹	/ Å	/°	/ Å	/ Å	/ Å	/ Å	/ Å	/ Å
HF/ 6-31G*	-5.4	1.988	166.5	0.951	0.953	+0.002	1.487	1.494	+0.007
HF/ 6-311G*	-7.0	1.955	179.0	0.943	0.945	+0.002	1.489	1.495	+0.006
B3LYP/ 6-31G*	-3.7	1.752	141.3	0.973	0.979	+0.006	1.500	1.508	+0.008
B3LYP/ 6-311G*	-9.3	1.699	164.7	0.966	0.974	+0.008	1.497	1.506	+0.009
B3LYP/ cc-pVTZ	-8.8	1.734	159.9	0.965	0.973	+0.008	1.496	1.505	+0.009
MP2/ 6-31G*	-10.4	1.835	137.2	0.977	0.981	+0.004	1.499	1.507	+0.008
[°] MP2/ 6-311+G**	-15.1	1.685	134.0	0.966	0.973	+0.007	1.491	1.502	+0.011
M06/ 6-31G*	-19.1	1.776	137.9	0.970	0.978	+0.008	1.495	1.507	+0.012
ωB97-D/ 6-31G*	-21.2	1.849	127.4	0.968	0.973	+0.005	1.498	1.508	+0.010

Table S2: Calculated complexation energies between *n*-trimethylsilane and perfluoro-*tert*-butanol, which are corrected for basis set superposition errors using the counterpoise method. Bond lengths and geometries for the minimised bound and free states are also shown.

^aDue to the size of this calculation, models in which the hexyl chains were replaced with ethyl groups were used.