## Supplementary Material

The proton chemical shift for protons transferred to the nitrogen base in PILs.

In the formation of a protic ionic liquid, the proton lowers its energy by leaving the weaker binding on the anion for the stronger interaction with the lone pair of the nitrogen base. If the anion is the weak base conjugate to a *strong* acid, then the proton is buried deep in the nitrogen lone pair and is well shielded, so the resonance is not far from that of the covalent reference TMS.
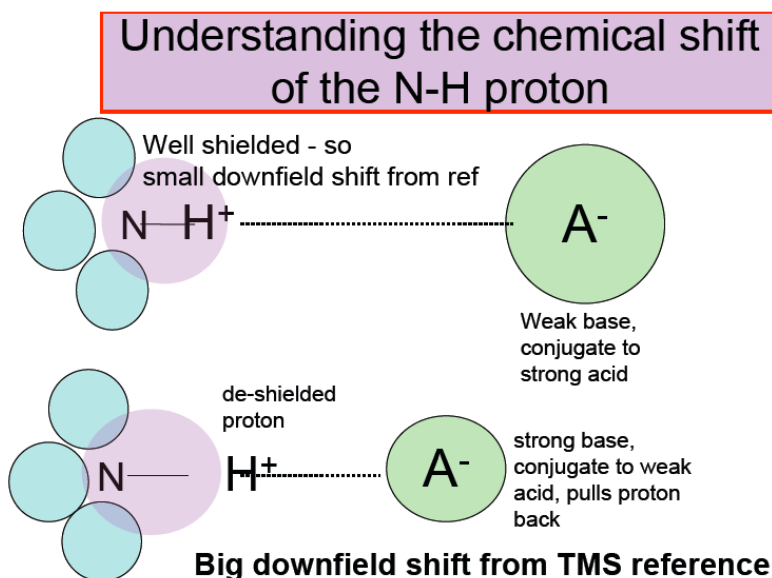
However if the base is stronger, e.g. acetate from the weak acid HAc, then the proton is more strongly withheld from the nitrogen lone pair electron density, and the proton will be DE-shielded, and so the resonance will move downfield. A table of N-H resonances, in compounds DEMAHX,

where DEMAH is diethylmethyl ammonium cation and X is an anion, is given below. In each case the resonance was shown by area integration to correspond to the lone proton on DEMA.

The water content, determined by Karl Fischer titration, is given in the table. When the water content is below 1000ppm there is essentially no effect on the value of the N-H chemical shift. It is important that the δ(N-H) value be determined in sufficiently anhydrous conditions.

The notion that the stronger the acid, the smaller is the downfield shift of the N-H proton, is well supported by this table, except for the (replicated but unexplained) position of the Olah superacid $HSbF_6$. Distortions from fluorous effects are under evaluation.

The two upper parts of the table are for strong bases DEMA, and trimethylamine TEA which have about the same base strength (judged from aqueous pKa data).

The lower two cases are for weaker bases (pyridine and picoline) and, as expected, the resonances move downfield because the base exerts a weaker "pull" on the proton - which can therefore move further away from electron density of the lone pair on the nitrogen.

N-H PMR chemical shifts for PILs formed from acids of differing acid strength. (Belieres, Byrne, and Angell (to be published)

A. for base diethylmethylamine (DEMA), pKa (aqueous) = 10.55

B. for base triethylamine, (TEA) pKa (aqueous) = 10.62

AlCl$_3$ and FeCl$_3$ convert water to HCl

Acid	ppm water in PIL	δ(N–H)/ppm	Acid	ppm water in PIL	δ(N–H)/ppm
HFeCl$_4$	low	No NMR	HFeCl$_4$	low	No NMR
HAlCl$_4$	low	4.618	HAlCl$_4$		4.956
HAlI$_4$	undetec	4.719 (110ºC)			
HTFSI	101	6.697	HTFSI	138	6.505
HBETI	183	6.65		219	6.437
HClO$_4$	31	7.010	HClO$_4$		6.074 (80°C)
HI		7.700 (110°C)			
HTf	24	7.771	HTf	22	7.732
H$_2$SO$_4$	211	8.391			
H$_2$Cl$_2$					
HBr					
HCl					
HSbF$_6$	469	8.56			

HCH$_3$SO$_3$	910	9.497	HCH$_3$SO$_3$	1291	9.374
HN(CN)$_2$	**1603**	9.501			
HNO$_3$	36	9.730			
HCl$_2$Ac	**1476**	10.245			
HTFAc	230	11.268	HTfAc	57	11.389
HAc	1306	14.0			

C. for base pyridine (Py)   **D. for base α–picoline (αCH$_3$Py)**

     pKa (aqueous) = 5.21   **pKa(aqueous) = 5.97**

(from Shuppert & CAA, JPC 1977)

HAl$_2$Cl$_7$ 0   9.2*

HAlCl$_4$ 0   9.8

H$_2$ZnCl$_4$ 10.8   H$_2$ZnCl$_4$ 10.6   (S&A)

H$_2$Cl$_2$ 12.3

HTf   12.8   (this wk)

HCl   13.5   13.5

* "free" pyridinium resonance is calculated to lie at 8.8 ppm (see above reference)