Supplementary Material (ESI) for Chemical Communications

Non-covalent interactions between iodo-perfluorocarbons and hydrogen bond acceptors

Rafel Cabot and Christopher A. Hunter*

SUPPLEMENTARY INFORMATION

NMR titrations

Association constants were determined using NMR titration protocols utilising an automated liquid handler to prepare the samples. The host solution was prepared at a concentration between 10 and 250 mM depending on the stability of the complex ([**1**] ~ 1/*K*). The guest stock solution was prepared by dissolving the guest in a sample of the host stock solution at a guest concentration between 500 mM and 2 M. Titration samples were prepared by mixing host and guest stock solutions in different proportions to obtain a saturation binding isotherm. ^{19}F-NMR spectra of each sample were recorded on a Bruker AMX400 spectrometer using an external D_2O capillary as deuterium lock signal. The observed changes in chemical shift of the host signals as a function of guest concentration were analysed using purpose-written software, which yields the association constant, the bound chemical shift and the free chemical shift.

Hydrogen Bond Parameters

Table S1. Hydrogen bond donor and acceptor parameters (α and β).

HBA		β_2^H	β
Tri-*n*-butylphosphine oxide	**2**	0.93	10.2
Quinuclidine	**3**	0.80	8.9
DABCO	**4**	0.81	8.9
Piperidine	**5**	0.74	8.3
Hexylamine	**6**	0.69	7.8
Diethylamine	**7**	0.70	7.9
Triethylamine	**8**	0.67	7.5
Pyridine	**9**	0.62	7.1
HBD [a]		α_2^H	α
4-fluorophenol		0.63	3.9
pyrrole		0.41	3.0

a M. H. Abraham, P. L. Grellier, D. V. Prior, P. P. Duce, J. J. Morris and P. J. Taylor, *J. Chem. Soc. Perkin Trans. 2*, **1989**, 699-711.

Experimental Verification of Hydrogen Bond Acceptor Parameters

Table S2. Association constants for formation of 1:1 complexes with **1** from NMR titrations in carbon tetrachloride at 295 K (experiment) and calculated using Equation 1 (predicted).

HBA	***HBD***	***log K_{expt}***	***log K_{pred}***
Quinuclidine	4-Fluorophenol	2.5 ± 0.1	2.6
Quinuclidine	Pyrrole	1.2 ± 0.1	1.3
Triethylamine	4-Fluorophenol	1.7 ± 0.2	2.0
Triethylamine	Pyrrole	0.8 ± 0.1	0.9

Crystallographic Data

Table S3. Crystallographic data for 25 crystal structures containing alkyl iodo-perfluorocarbons involved in halogen bonds (obtained from the Cambridge Crystallographic Data Centre).

Refcode	**d N-I (Å)**	**d C-I (Å)**	**CCDC ref**	**HBD**	**pK_a**
DENMIT	2.746	2.164	604155	Pyridine	5
IHUNOO	2.858	2.156	214349	Pyridine	5
LEZPIQ	2.863	2.111	618383	Pyridine	5
LEZPOW	2.961	2.095	618384	Pyridine	5
LEZPUC	2.831	2.131	618385	Pyridine	5
LEZPUC01	2.841	2.139	618386	Pyridine	5
LEZQAJ	2.806	2.101	618387	Pyridine	5
LOQBAU	2.842	2.162	-	Pyridine	5
QANRUS	2.839	2.149	-	Pyridine	5
ULOKUB	2.928	2.152	214919	Pyridine	5
XUHNUJ	2.771	2.155	187509	Pyridine	5
PIFVOQ	2.832	2.170	625929	Pyridine	5
PIFVUW	2.855	2.158	625930	Pyridine	5
PIFWAD	2.756	2.155	625931	Pyridine	5
LOSVAQ	2.861	2.186	141920	NHR_2	11
QANSED	2.807	2.206	-	NHR_2	11
ACIREK	2.799	2.177	215347	Alkyl-NR_2	10
AXAGUB	2.722	2.145	221831	Alkyl-NR_2	10
JALQIW	2.862	2.135	-	Alkyl-NR_2	10
JALQIW01	2.825	2.200	-	Alkyl-NR_2	10
JALQOC	2.797	2.193	-	Alkyl-NR_2	10
XOMLUG	2.762	2.169	164105	Alkyl-NR_2	10
LAKGAG	2.836	2.158	259450	Aryl-NR_2	1
XAKGIA	2.847	2.158	256351	Aryl-NR_2	1
ULOKEL	2.817	2.175	214916	*N*-Me morpholine	7.4

R represents an alkyl group
pK_a values from pK_a Values for Aqueous Solutions and DMSO (D. H. Ripin, D. A. Evans) and pK_a Values for Aqueous Solutions (W. P. Jencks, F. H. Westheimer)
http://daecr1.harvard.edu/pdf/evans_pKa_table.pdf
http://research.chem.psu.edu/brpgroup/pKa_compilation.pdf

Computational methods

Semi-empirical AM1 and Ab initio 3-21G(*) calculations were performed using Spartan '06 Wavefunction, Inc., Irvine, CA, USA.

Table S4. Hartree Fock 3-21G(*) HOMO and LUMO energies (eV), pK_a values and relative rates of the Menschutkin reaction for hydrogen bond acceptors.

	2	**3**	**4**	**5**	**6**	**7**	**8**	**9**
E HOMO (eV)	-10.37	-8.78	-8.08	-9.34	-9.11	-9.44	-9.83	-9.69
E LUMO (eV)	5.96	6.38	6.44	7.01	7.10	7.26	7.15	3.54
pK_a		11.0	8.8	11.2	10.5	11.0	10.7	5.3
k_{rel}		5940	3665				93	1