Supplementary material
Hydrogen-bond strengths by magnetically induced currents†

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1 Current strength evaluation

The critical points along and in the vicinity of an H-bond were studied, to obtain a representative current strength passing the bond of interest and to avoid induction of ring currents circulating around the complete H-bonded dimer. This behaviour was investigated by applying the external magnetic field in different directions relative to the molecular plane. Ring currents were avoided when the external magnetic field was set parallel to the molecular plane. For consistency, the same procedure was applied for all H-bonded dimers used in the linear fit.

The placement and size of the integration domain perpendicular to the studied H-bond was chosen such that spurious current contributions from neighbouring atoms as well as edge currents circulating around the monomer are avoided. This was realised in two steps. First, the current strength passing the bond was integrated in discrete spatial points along the H-bond using a rectangular integration plane of 6-8 bohr (1 bohr = 0.529Å). The integration plane was then placed at the position where the minimum current strength was obtained. In the second step, the width of the integration plane was varied, while the height was kept fixed at 10 bohr. The current strength as a function of the width showed two minima which define the beginning and the end of the final integration domain, yielding the data in Fig. 1 of the main paper.

2 Employed fit set and error estimation

Table 1 shows the calculated H-bond energies and current strengths, used as input for the linear fit. The linear regression was obtained with gnuplot[1] using a least squares fit procedure

$$J_{\mathrm{dia}}(E) = aE + b\,. \tag{1}$$

The respective constants a and b are given in Table 2 , together with standard deviations of the fitting error. The squared linear correlation coefficient of the curves are $r^2_{BP86} = 0.83$, $r^2_{B3LYP} = 0.86$, $r^2_{MP2} = 0.84$. The expected error of the method for an H-bond of strength E was estimated as,

$$\Delta E = \frac{1}{a}\sqrt{E^2(\Delta a)^2 + (\Delta b)^2}, \tag{2}$$

which gives for the B3LYP calculations an expected error of,

$$\Delta E_{\mathrm{B3LYP}} = \frac{\sqrt{0.0001E^2 + 0.006}}{0.078}. \tag{3}$$

A linear relation between intramolecular hydrogen bond strengths and proton shieldings has recently been described in other work.[2,3] Figures 2 and 3 of the main manuscript were prepared using VMD.[4]

References

1 http://www.gnuplot.info/.
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Table 1 Calculated H-bond energies in kcal/mol and current strengths in nA/T for H-bonded dimers. In all calculations, the def2-TZVPP basis set has been applied.

dimer	method	R_{X-H} pm	H-bond energy in kcal/mol	J_{dia} in nA/T
NH_3-NH_3	BP86	225.82	-2.74	0.7
	B3LYP	231.03	-2.85	0.6
	MP2	226.83	-3.37	0.6
NH_3-HF	BP86	164.94	-13.77	1.5
	B3LYP	169.03	-13.29	1.3
	MP2	169.80	-12.83	1.1
NH_3-HCl	BP86	164.60	-10.31	1.0
	B3LYP	176.57	-8.82	1.0
	MP2	178.25	-9.12	0.7
NH_3-H_2O	BP86	193.70	-6.57	1.1
	B3LYP	198.80	-6.47	1.0
	MP2	197.68	-6.77	0.8
H_2O-HF	BP86	167.67	-9.37	1.2
	B3LYP	170.39	-9.43	1.1
	MP2	171.10	-9.12	0.9
H_2O-HCl	BP86	179.00	-6.09	1.0
	B3LYP	187.65	-5.68	0.9
	MP2	187.70	-6.08	0.7
H_2O-H_2O	BP86	193.16	-4.93	0.9
	B3LYP	196.00	-5.16	0.8
	MP2	195.29	-5.37	0.7
HCHO-NH_3	BP86	232.63	-2.51	0.5
	B3LYP	234.80	-3.01	0.4
	MP2	226.96	-4.01	0.5
HCHO-HF	BP86	168.95	-8.02	1.0
	B3LYP	171.98	-8.29	1.0
	MP2	172.32	-8.35	0.8
HCHO-HCl	BP86	179.26	-5.07	0.9
	B3LYP	189.03	-4.83	0.8
	MP2	185.49	-5.92	0.7
HCHO-H_2O	BP86	197.17	-4.11	0.7
	B3LYP	200.80	-4.58	0.5
	MP2	198.76	-5.45	0.6

Table 2 Calculated fit constants a [nA mol kcal^{-1} T^{-1}] and b [nA T^{-1}] according to equation 1 and asymptotic standard error in %.

method	a	b	Δa in %	Δb in %
BP86	-0.0703814	0.477962	14.86	16.28
B3LYP	-0.0780517	0.344827	13.31	21.76
MP2	-0.0550801	0.349201	14.65	17.13