Electronic Supplementary Information (ESI)

Spin-orbit coupling as a probe to decipher halogen bonding

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Table S1 Counterpoise corrected interaction energy (kcal/mol) for XY···NH_3 complexes (X, Y = At, I) at various level of theory

	sr-B3LYP/AVTZ	**2c-B3LYP/AVTZ**	**sr-HSE06/AVTZ**	**2c-HSE06/AVTZ**	**sr-MP2/AV5Z**[a]	**2c-MP2/AV5Z**[a]
At–At···NH_3	-9.14	-6.78	-11.17	-8.85	-10.15	-8.38
I–At···NH_3	-10.44	-9.57	-12.55	-11.67	-11.58	-10.99
I–I···NH_3	-7.89	-7.65	-9.74	-9.51	-8.53	-8.40
At–I···NH_3	-6.70	-4.48	-8.46	-6.19	-7.27	-5.46

[a] The single point RI-MP2 calculations were carried out with the TURBOMOLE program package on top of the previously optimized PW6B95 geometries. The ECP28MDF and ECP60MDF were used for iodine and astatine atoms, respectively, in conjunction with the aug-cc-pV5Z-PP basis set supplemented by the 2c extensions described in ref. 50. The aug-cc-pV5Z basis set was used for the remaining atoms. The results also rely on the frozen-core approximation (*e.g.* the 5s5p5d electrons of At were kept frozen as well as the 1s electrons of N).

Table S2 QTAIM properties of AtY species (Y = At, I, Br, Cl, F) obtained at the 2c-PW6B95/AVTZ level of theory

	Integrated property	At the bond critical point		
	q(At)[b]	$\rho_b.10^2$ [c]	$\nabla^2\rho_b.10^2$ [d]	$\lvert V_b\rvert/G_b$ [e]
At_2	–	4.6	3.0	1.59
ΔSO[a]	–	-1.8	+0.9	-0.20
AtI	+0.19	6.1	2.9	1.69
ΔSO[a]	+0.10	-0.9	+1.3	-0.16
AtBr	+0.31	7.1	6.0	1.58
ΔSO[a]	+0.06	-1.0	+1.2	-0.11
AtCl	+0.43	8.0	9.7	1.51
ΔSO[a]	+0.05	-1.2	+0.6	-0.08
AtF	+0.64	10.9	36.9	1.28
ΔSO[a]	+0.02	-1.6	-5.2	-0.02

[a] The spin-orbit effects are defined as the difference between the results of 2c- and sr-calculations. [b] At atomic charge (a.u.). [c] Electron density (a.u.). [d] Laplacian of the electron density (a.u.). [e] Ratio between the potential energy density (V_b) and the positive definite kinetic energy density (G_b).

Table S3 Spectroscopic constants of AtY species (Y = At, I, Br, Cl, F) calculated at the 2c-PW6B95/AVTZ level of theory

		R_e (Å)	ω_e (cm^{-1})
At_2		2.995	117
	ΔSO[a]	+0.151	-44
AtI		2.836	163
	ΔSO[a]	+0.085	-29
AtBr		2.635	212
	ΔSO[a]	+0.075	-33
AtCl		2.491	313
	ΔSO[a]	+0.075	-50
AtF		2.067	515
	ΔSO[a]	+0.058	-73

[a] The spin-orbit effects are defined as the difference between the results of 2c- and sr-calculations.

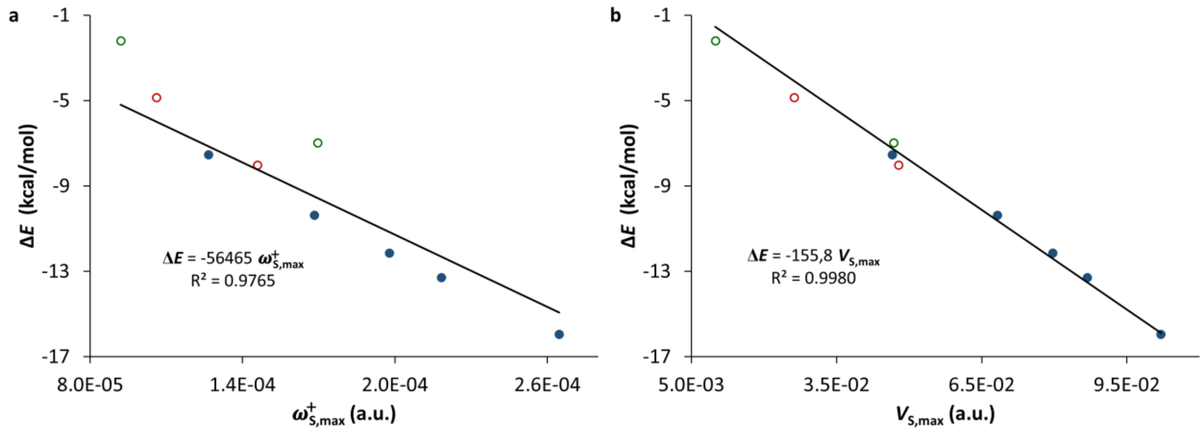

Fig. S1 Correlations at the 2c-PW6B95/AVTZ level of theory between the interaction energy in the X–Y···NH_3 complexes and the $\omega^{+}_{S,max}$ (**a**) and $V_{S,max}$ (**b**) values at the Y atom in XY monomers (the XB interaction is mediated by the Y halogen element). Color code: blue circles for Y = At, red circles for Y = I, and green circles for Y = Br.