Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information (ESI)

Delocalized relativistic effects, from the viewpoint of halogen bonding

Serigne Sarr, Jérôme Graton, Seyfeddine Rahali, Gilles Montavon, and Nicolas Galland

Contents

Figures

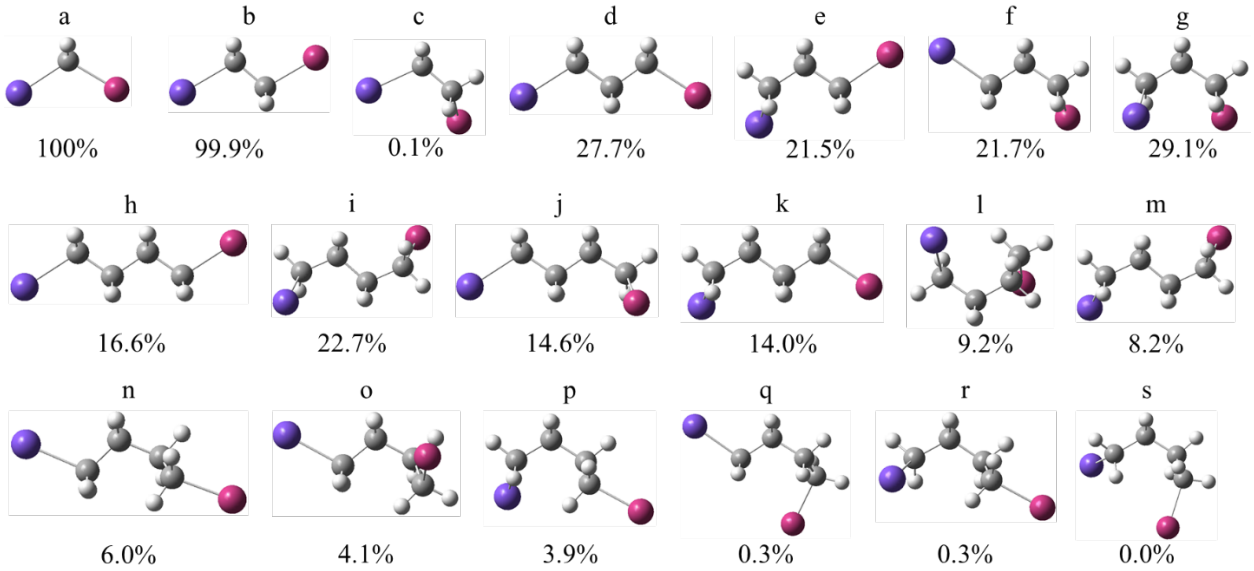

Fig. S1 Optimized structures and calculated Boltzmann populations at the 2c-B3LYP/TZVPD level of theory for the different conformers of the At–R–I dihalogenated alkanes derived from methane (a), ethane (b-c), propane (d-g) and butane (h-s). Atom's color code: purple for At, pink for I, grey for C and white for H.

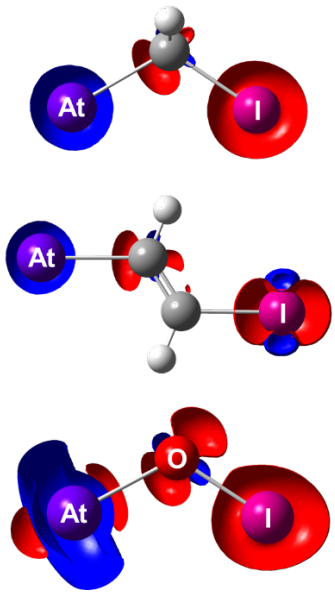

Fig. S2 Difference between electron densities obtained from 2c- and sr-B3LYP/TZVPD calculations, on the 2c-B3LYP/TZVPD optimized geometries of At–CH_2–I (top), *E*-At–CH=CH–I (middle) and At–O–I (bottom) species. The surfaces (isovalue = 0.00115 a.u.) in red color show the regions with a significant increase of electron density and in blue color the regions with a significant decrease.

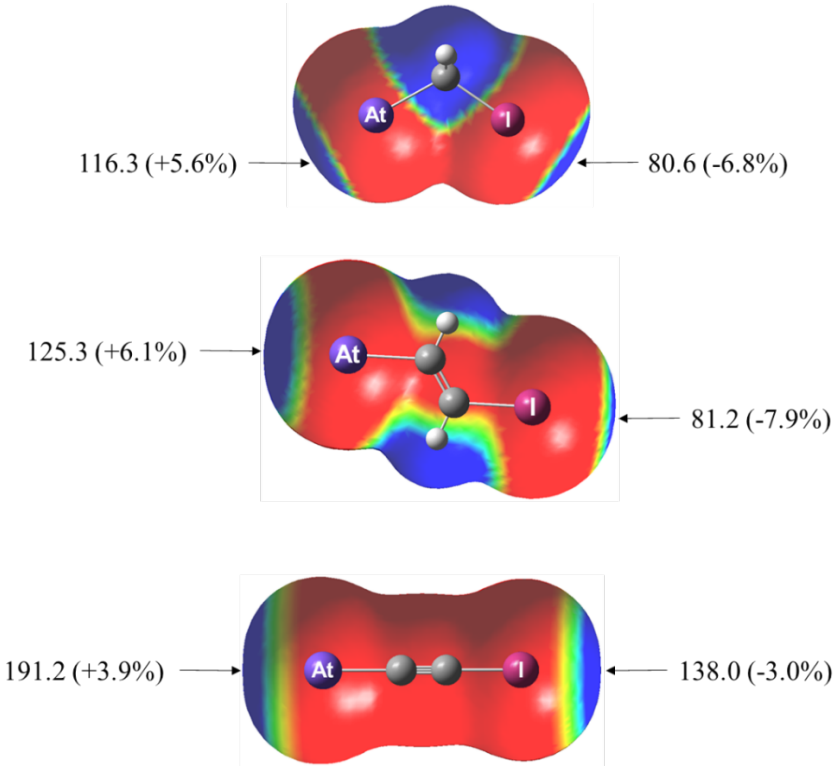

Fig. S3 2c-B3LYP/TZVPD calculated electrostatic potential at the At–CH_2–I (top), *E*-At–CH=CH–I (middle) and At–C≡C–I (bottom) molecular surfaces (defined by 0.001 a.u. density isosurfaces). The maximum values, $V_{S,max}$, at the astatine and iodine σ-holes are in kJ mol^{-1} (SOC effects are given in parenthesis). Color code: from red (lowest values) to blue (highest values).

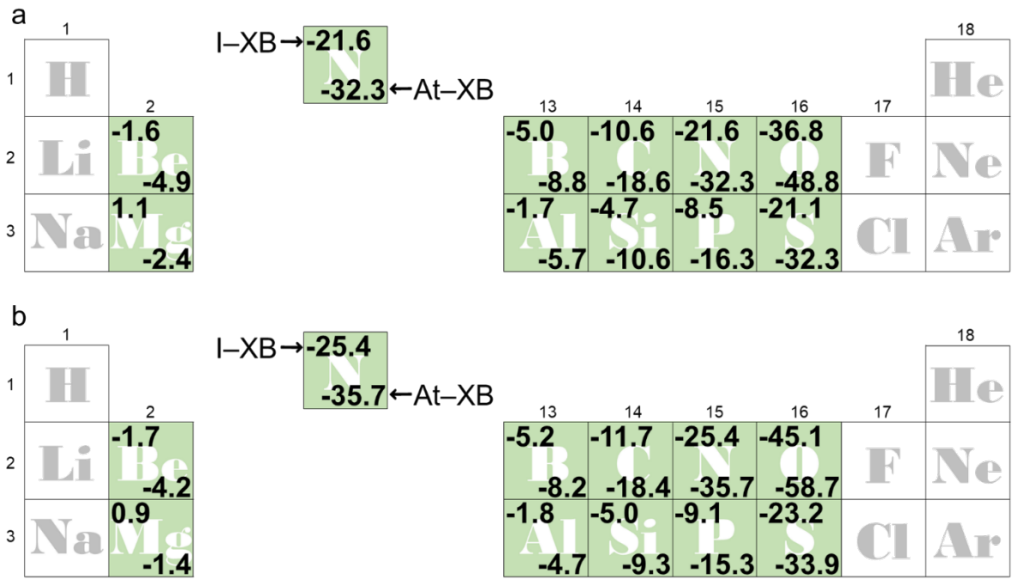

Fig. S4 Interaction energies (kJ/mol) for the XB complexes formed between NH_3 and At–AH_n–I species (A = Be, B, C, N, O, Mg, Al, Si, P, S and n = 0, 1, 2), calculated at the 2c-B3LYP/TZVPD (a) and sr-B3LYP/TZVPD (b) levels of theory.

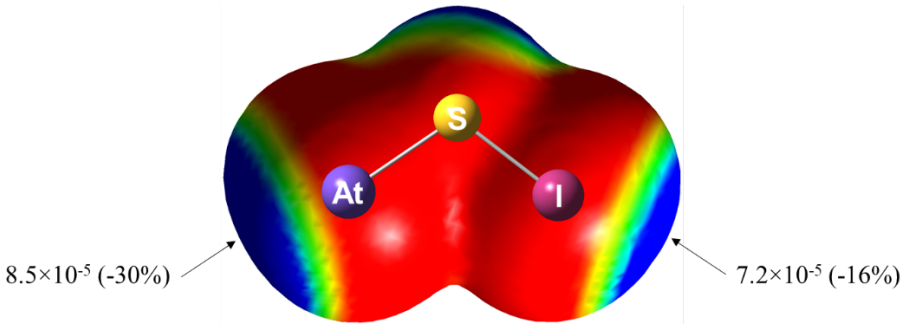

Fig. S5 2c-B3LYP/TZVPD calculated local electrophilicity at the At–S–I molecular surface (defined by the 0.001 a.u. density isosurface). The most positive electrophilicity values, $\omega^{+}_{S,max}$, at the astatine and iodine σ-holes are in a.u (SOC effects are given in parenthesis). Color code: from red (lowest values) to blue (highest values).

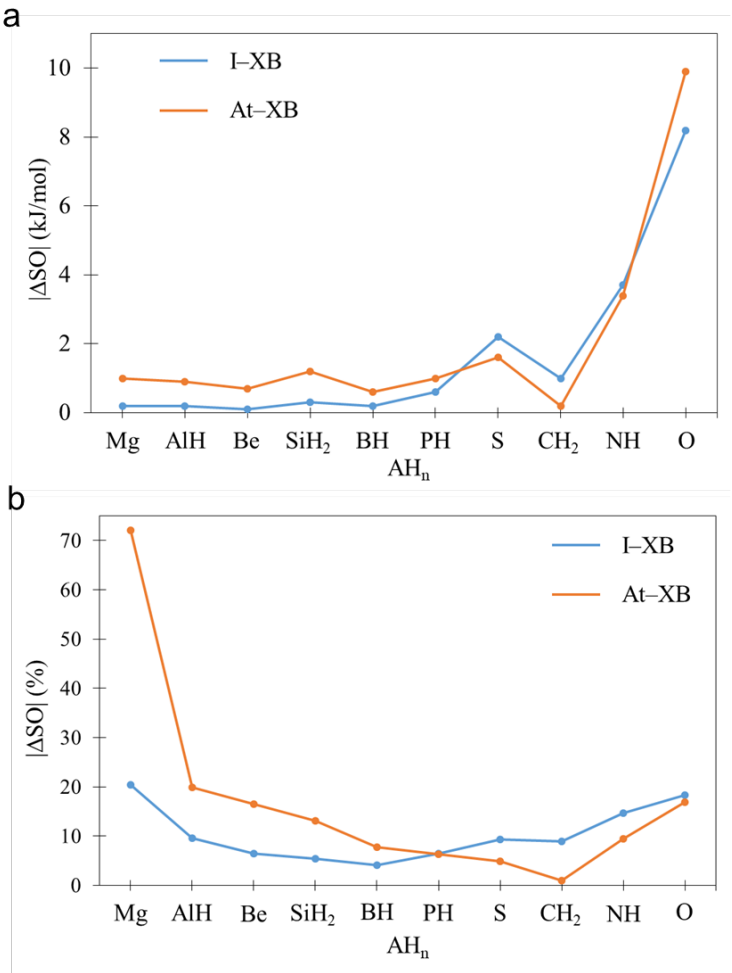

Fig. S6 Spin-orbit coupling effects (ΔSO) in kJ/mol (a) and in relative value (b) on the computed interaction energies at the B3LYP/TZVPD level of theory for the XB complexes formed between ammonia and At–AH_n–I species, with the atom A of increasing electronegativity.

Tables

Table S1 Boltzmann populations (in %) of the XB complexes formed by the conformers stemmed from ethane, propane and butane, according to BSSE corrected energies at the 2c-B3LYP/TZVPD level of theory.

	ethane		propane				butane	
conformer[a]	b	c	d	e	f	g	h	i
I-XB	0.2	99.8	33.6	19.7	21.0	25.7	53.1	46.9
At-XB	0.1	99.9	44.1	19.6	17.2	19.1	59.3	40.7

[a] Same notation as in Fig. S1.

Table S2 sr-B3LYP/TZVPD interaction energies and distances, C–X distances and their respective variations upon complexation (X = I, At), for the complexes formed between the dihalogenated alkanes and the trimethylamine N-oxide.

		ΔE (kJ/mol)	d_{int} (Å)	r_{XB}[a]	$d_{C–X}$ (Å)	$\Delta d_{C–X}$ (Å)
At–CH_2–I	I–XB	-22.2	2.824	0.806	2.156	0.010
	At–XB	-31.9	2.786	0.787	2.273	0.017
At–$(CH_2)_2$–I[b]	I–XB	-15.9	2.901	0.829	2.209	0.006
	At–XB	-24.8	2.849	0.805	2.312	0.013
At–$(CH_2)_3$–I[b]	I–XB	-13.5	2.957	0.845	2.189	0.006
	At–XB	-21.5	2.899	0.819	2.295	0.011
At–$(CH_2)_4$–I[b]	I–XB	-11.9	2.988	0.854	2.191	0.004
	At–XB	-19.3	2.927	0.827	2.295	0.009
E-At–CH=CH–I	I–XB	-21.1	2.841	0.812	2.128	0.015
	At–XB	-31.3	2.797	0.790	2.23519	0.025
At–$(CH=CH)_2$–I	I–XB	-17.3	2.903	0.829	2.112	0.018
	At–XB	-26.1	2.851	0.805	2.222	0.027
At–$(CH=CH)_3$–I	I–XB	-17.5	2.894	0.827	2.103	0.009
	At–XB	-26.4	2.845	0.804	2.211	0.018
At–C≡C–I	I–XB	-34.5	2.715	0.776	2.033	0.038
	At–XB	-49.3	2.674	0.755	2.151	0.056
At–$(C≡C)_2$–I	I–XB	-37.3	2.700	0.771	2.024	0.038
	At–XB	-51.9	2.664	0.753	2.143	0.056
At–$(C≡C)_3$–I	I–XB	-39.5	2.685	0.767	2.022	0.324
	At–XB	-54.2	2.652	0.749	2.142	0.057

[a] Normalized interaction distance $r_{XB} = \frac{d_{int}}{r_O + r_X}$; r_O and r_X are the van der Waals radii of the O and X atoms, respectively. A radius of 2.02 Å is assumed for astatine according to sr calculations. [b] Weighted values based on the calculated Boltzmann populations for each set of XB complexes.

Table S3 B3LYP/TZVPD interaction energies and distances, C–I distances and their respective variations upon complexation, for the complexes formed between R–I species and trimethylamine N-oxide.

		ΔE (kJ/mol)	d_{int} (Å)	r_{XB}[a]	$d_{C–I}$ (Å)	$\Delta d_{C–I}$ (Å)
	2c	-12.7	2.966	0.848	2.177	0.011
H–CH_2–I	sr	-12.5	2.968	0.848	2.172	0.011
	ΔSO	-0.2 (-1%)	-0.002	0.000	0.005	0.000
	2c	-9.4	3.027	0.865	2.196	0.003
H–$(CH_2)_4$–I[b]	sr	-9.3	3.030	0.866	2.191	0.003
	ΔSO	-0.1 (-2%)	-0.003	-0.001	0.005	0.000
	2c	-15.6	2.930	0.837	2.120	0.009
H_2C=CH–I	sr	-15.4	2.932	0.838	2.116	0.009
	ΔSO	-0.2 (-1%)	-0.002	-0.001	0.004	0.000
	2c	-16.5	2.908	83.1	2.108	0.009
H–$(CH=CH)_3$–I	sr	-16.3	2.910	0.831	2.104	0.009
	ΔSO	-0.2 (-1%)	-0.002	0.000	0.004	0.000
	2c	-34.5	2.724	0.778	2.038	0.037
H–C≡C–I	sr	-34.3	2.725	0.779	2.033	0.037
	ΔSO	-0.2 (-1%)	-0.002	-0.001	0.005	0.000
	2c	-41.1	2.677	0.765	2.028	0.039
H–$(C≡C)_3$–I	sr	-40.8	2.678	0.765	2.023	0.039
	ΔSO	-0.3 (-1%)	-0.002	0.000	0.005	0.000

[a] Normalized interaction distance $r_{XB} = \frac{d_{int}}{r_O + r_X}$; r_O and r_X are the van der Waals radii of the O and X atoms, respectively. A radius of 2.02 Å is assumed for astatine according to sr calculations. [b] Weighted values based on the calculated Boltzmann populations for each set of XB complexes.

Table S4 B3LYP/TZVPD interaction energies and distances, C–X distances and their respective variations upon complexation (X = I, At), for the complexes formed between the At–CH=CH–I isomers and the trimethylamine N-oxide.

			ΔE (kJ/mol)	d_{int} (Å)	r_{XB}[a]	$d_{C–X}$ (Å)	$\Delta d_{C–X}$ (Å)
		2c	-20.3	2.851	0.815	2.117	0.011
	I-XB	sr	-21.6	2.839	0.811	2.108	0.013
		ΔSO	1.3 (6%)	0.012	0.003	0.009	-0.002
Z-At–CH=CH–I							
	At-XB	2c	-33.2	2.796	0.790	2.260	0.025
		sr	-31.9	2.795	0.790	2.217	0.024
		ΔSO	-1.4 (-4%)	0.001	0.000	0.043	0.001
		2c	-19.7	2.855	0.816	2.138	0.012
	I-XB	sr	-21.1	2.841	0.812	2.128	0.015
		ΔSO	1.4 (7%)	0.013	0.004	0.010	-0.003
E-At–CH=CH–I							
	At-XB	2c	-32.6	2.799	0.791	2.280	0.025
		sr	-31.3	2.797	0.790	2.235	0.025
		ΔSO	-1.3 (-4%)	0.002	0.001	0.045	0.001

[a] Normalized interaction distance $r_{XB} = \frac{d_{int}}{r_O + r_X}$; r_O and r_X are the van der Waals radii of the O and X atoms, respectively. A radius of 2.02 Å is assumed for astatine according to sr calculations.

Table S5 Interaction energies (kJ/mol) of the XB complexes formed by At–CH_2–I, *E*-At–CH=CH–I and At–C≡C–I XB-donors with Me_3NO at the PW6B95/TZVPD and MP2/TZVPPD levels of theory.

			PW6B95/TZVPD	**MP2/TZVPPD**[a]
At–CH_2–I	I-XB	2c	-26.7	-31.6
		sr	-28.5	-33.0
		ΔSO	1.8 (6%)	1.4 (4%)
	At-XB	2c	-40.0	-44.0
		sr	-39.3	-44.0
		ΔSO	-0.7 (-2%)	0.0 (0%)
E-At–CH=CH–I	I-XB	2c	-25.6	-30.2
		sr	-26.9	-31.3
		ΔSO	1.3 (5%)	1.1 (3%)
	At-XB	2c	-39.2	-42.9
		sr	-38.0	-42.4
		ΔSO	-1.2 (-3%)	-0.5 (-1%)
At–C≡C–I	I-XB	2c	-39.4	-43.6
		sr	-40.6	-44.6
		ΔSO	1.2 (3%)	1.0 (2%)
	At-XB	2c	-57.7	-60.5
		sr	-56.3	-60.1
		ΔSO	-1.4 (-2%)	-0.4 (-1%)

[a] Single point calculations performed on PW6B95/TZVPD optimized geometries.

Table S6 2c-B3LYP/TZVPD interaction distances and angles (Θ_{AXN} with X = I or At) for the complexes formed between the At–AH_n–I species and the NH_3 Lewis base.

		d_{int} (Å)	r_{XB}[a]	Θ_{AXN} (°)
At–O–I	I-XB	2.693	0.769	176.1
	At-XB	2.732	0.772	176.8
At–NH–I	I-XB	2.877	0.822	175.7
	At-XB	2.865	0.809	176.3
At–CH_2–I	I-XB	3.141	0.897	178.3
	At-XB	3.060	0.864	179.5
At–S–I	I-XB	2.895	0.827	177.1
	At-XB	2.874	0.812	177.9
At–PH–I	I-XB	3.224	0.921	176.5
	At-XB	3.111	0.879	177.8
At–BH–I	I-XB	3.513	1.004	178.8
	At-XB	3.405	0.962	178.9
At–SiH_2–I	I-XB	3.466	0.990	179.1
	At-XB	3.299	0.932	179.3
At–Be–I	I-XB	3.804	1.087	180.0
	At-XB	3.619	1.022	180.0
At–AlH–I	I-XB	3.743	1.069	179.6
	At-XB	3.541	1.000	179.6
At–Mg–I	I-XB	4.120	1.177	180.0
	At-XB	3.715	1.050	180.0

[a] Normalized interaction distance $r_{XB} = \frac{d_{int}}{r_N + r_X}$; r_N and r_X are the van der Waals radii of the N and X atoms, respectively. A radius of 2.02 Å is assumed for astatine according to sr calculations.

Table S7 Interaction energies (kJ/mol) of the XB complexes formed by At–BH–I, At–CH_2–I, At–NH–I and At–O–I with the NH_3 Lewis base at the PW6B95/TZVPD and MP2/TZVPPD levels of theory.

			PW6B95/TZVPD	**MP2/TZVPPD**[a]
At–BH–I	I-XB	2c	-7.1	-8.3
		sr	-7.3	-8.5
		ΔSO	0.2 (3%)	0.2 (2%)
	At-XB	2c	-11.3	-12.2
		sr	-10.2	-11.5
		ΔSO	-1.1 (-11%)	-0.7 (-6%)
At–CH_2–I	I-XB	2c	-13.2	-13.7
		sr	-14.2	-14.5
		ΔSO	1.0 (7%)	0.8 (5%)
	At-XB	2c	-21.8	-21.6
		sr	-21.5	-21.6
		ΔSO	-0.3 (-1%)	0.0 (0%)
At–NH–I	I-XB	2c	-24.7	-24.6
		sr	-28.4	-27.3
		ΔSO	3.7 (13%)	2.7 (10%)
	At-XB	2c	-36.5	-34.2
		sr	-38.2	-37.3
		ΔSO	1.7 (5%)	3.1 (8%)
At–O–I	I-XB	2c	-40.3	-40.2
		sr	-48.8	-46.9
		ΔSO	8.5 (17%)	6.7 (14%)
	At-XB	2c	-53.6	-50.6
		sr	-63.6	-60.7
		ΔSO	10.0 (16%)	10.1 (17%)

[a] Single point calculations performed on PW6B95/TZVPD optimized geometries.

Structures

Cartesian coordinates (Å) of the XB complexes formed between the At–AH_n–I species and ammonia at the 2c-B3LYP/TZVPD level of theory.

At–BH–I···NH_3

N	5.238011	-0.987390	0.000000
H	5.230869	-2.001649	0.000001
H	5.763272	-0.692158	0.815905
H	5.763271	-0.692159	-0.815905
I	1.967107	0.293873	0.000000
At	-1.854174	-0.153937	-0.000000
B	0.012865	1.105798	0.000001
H	-0.139720	2.278066	0.000001

I–BH–At···NH_3

N	4.386146	-0.979607	0.000033
H	4.407274	-1.992803	0.043278
H	4.915485	-0.634904	0.793671
H	4.889481	-0.705119	-0.836745
At	1.186503	0.185293	-0.000011
I	-2.644580	-0.239450	0.000002
B	-0.907026	0.993288	0.000059
H	-1.070123	2.164573	0.000131

At–CH_2–I···NH_3

N	-4.804331	-1.057468	0.000001
H	-5.542484	-0.362375	0.001722
H	-4.934382	-1.643620	0.817067
H	-4.935667	-1.640935	-0.818778
C	-0.036642	1.236575	0.000003
H	0.057635	1.833942	0.897702
H	0.057636	1.833947	- 0.897693
At	1.798582	-0.168508	0.000000
I	-1.957207	0.269530	-0.000001

I–CH_2–At···NH_3

N	-4.001333	-1.055006	0.000000
H	-4.731549	-0.351520	- 0.000001
H	-4.137260	-1.638366	0.818189
H	-4.137259	-1.638367	-0.818188
C	0.906590	1.123227	0.000000
H	0.999200	1.723586	0.896305
H	0.999200	1.723587	-0.896304
At	-1.199999	0.176684	0.000000
I	2.558063	-0.267762	-0.000000

At–NH–I···NH_3

N	-3.728363	0.917093	0.042810
H	-3.878320	1.435199	0.900921
H	-4.409848	0.167859	0.003768
H	-3.901620	1.541159	-0.736874
N	0.890363	-0.947872	-0.322691
H	0.866055	-1.753155	0.307225
I	-1.048658	-0.122657	-0.084891
At	2.535799	0.272716	0.638246

I–NH–At···NH_3

N	3.749934	-1.045194	0.022844
H	4.013591	-1.267387	0.976212
H	4.434532	-0.396140	-0.348506
H	3.799023	-1.898284	-0.522825
At	1.108994	0.061368	-0.085735
N	-0.966024	0.986285	-0.308374
H	-0.920367	1.772248	0.343894
I	-2.509911	-0.167123	0.541190

At–O–I···NH_3

N	-4.372990	0.830028	0.000000
H	-4.338158	1.842841	-0.000000
H	-4.879280	0.524422	0.822929
H	-4.879280	0.524422	-0.822929
O	-0.057973	-1.103984	-0.000000
I	-1.884109	-0.198574	-0.000000
At	1.706226	0.125346	0.000000

I–O–At···NH_3

N	3.712397	-0.822199	0.000000
H	3.713050	-1.836097	0.000000
H	4.214134	-0.504259	0.821641
H	4.214134	-0.504259	-0.821641
O	-0.862106	1.016801	0.000000
I	-2.437863	-0.204469	-0.000000
At	1.152653	0.132970	0.000000

At–O–I···NH_3

N	-4.372990	0.830028	0.000000
H	-4.338158	1.842841	-0.000000
H	-4.879280	0.524422	0.822929
H	-4.879280	0.524422	-0.822929
O	-0.057973	-1.103984	-0.000000
I	-1.884109	-0.198574	-0.000000
At	1.706226	0.125346	0.000000

I–O–At···NH_3

N	3.712397	-0.822199	0.000000
H	3.713050	-1.836097	0.000000
H	4.214134	-0.504259	0.821641
H	4.214134	-0.504259	-0.821641
O	-0.862106	1.016801	0.000000
I	-2.437863	-0.204469	-0.000000
At	1.152653	0.132970	0.000000

At–Mg–I···NH_3

N	-4.861703	0.058320	-0.000151
H	-5.232422	1.002400	0.000593
H	-5.241773	-0.410350	0.815088
H	-5.242466	-0.409334	-0.815650
Mg	1.807044	0.014178	0.000098
I	-0.741928	0.031001	0.000126
At	4.464555	-0.003443	-0.000104

I–Mg–At···NH_3

N	-4.705294	0.058007	0.000696
H	-5.074854	1.002227	0.026246
H	-5.084754	-0.432230	0.803463
H	-5.084684	-0.388092	- 0.827453
Mg	1.665079	0.014357	-0.001030
At	-0.989904	0.032598	-0.000066
I	4.225532	-0.003372	-0.001856

At–AlH–I···NH_3

N	5.707945	-1.240858	0.000000
H	5.639867	-2.252816	0.000000
H	6.250496	-0.978475	0.815755
H	6.250496	-0.978475	-0.815755
I	2.280498	0.262623	0.000000
Al	0.012856	1.274804	0.000000
H	-0.161106	2.835498	0.000000
At	-2.105516	-0.240367	0.000000

I–AlH–At···NH_3

N	-4.720444	1.167895	-0.000001
H	-4.694400	2.181879	-0.000004
H	-5.251122	0.882646	0.815979
H	-5.251124	0.882641	-0.815977
At	-1.437650	-0.159373	-0.000001
Al	0.964272	-1.148594	-0.000001
H	1.224168	-2.698431	-0.000003
I	2.956233	0.359518	0.000002

At–PH–I···NH_3

N	4.958760	-1.325414	0.016617
H	4.896734	-2.208944	-0.477100
H	5.273514	-1.525042	0.959607
H	5.680077	-0.774221	-0.435153
P	0.015931	1.534459	-0.086629
H	-0.031634	1.754631	1.314908
At	-1.925631	-0.267883	0.001118
I	2.130371	0.222351	-0.005173

I–PH–At···NH_3

N	4.143445	-1.240125	0.023654
H	4.616237	-1.114358	0.911835
H	4.749878	-0.872908	-0.701363
H	4.046997	-2.237290	-0.133488
At	1.358575	0.146201	-0.005232
P	-0.973609	1.401988	-0.081793
H	-1.001357	1.621667	1.320347
I	-2.684728	-0.418362	0.002051

At–SiH_2–I···NH_3

N	-5.288248	-1.317644	-0.000026
H	-5.414550	-1.879226	0.835025
H	-6.059876	-0.660636	-0.039051
H	-5.382826	-1.938846	-0.796143
Si	-0.010530	1.381870	-0.000026
H	0.094533	2.218399	-1.213179
H	0.094550	2.218457	1.213085
I	-2.192242	0.240513	0.000016
At	2.000260	-0.268565	-0.000000

I–SiH_2–At···NH_3

N	-4.404482	-1.212471	0.000001
H	-4.542154	-1.797901	0.816720
H	-5.142706	-0.517001	-0.000003
H	-4.542152	-1.797905	-0.816716
At	-1.399049	0.146873	0.000001
I	2.799796	-0.405807	-0.000001
Si	0.953443	1.247551	0.000001
H	1.120071	2.078962	-1.210777
H	1.120072	2.078960	1.210780

At–S–I···NH_3

N	4.632419	1.230466	0.000001
H	5.177025	0.991869	0.820879
H	4.484962	2.233323	0.000003
H	5.177022	0.991873	-0.820880
S	0.036684	-1.484404	0.000004
I	2.106375	-0.183931	0.000002
At	-1.876362	0.243159	-0.000002

I–S–At···NH_3

N	3.921700	1.146116	-0.000000
H	4.456383	0.884563	0.820774
H	3.821613	2.155112	-0.000528
H	4.456790	0.883745	-0.820248
S	-0.951108	-1.362708	-0.000000
I	-2.627118	0.387522	0.000000
At	1.344333	-0.125665	0.000000

At–Be–I···NH_3

N	-4.567106	0.052880	-0.000002
H	-4.939064	0.996514	0.000001
H	-4.946454	-0.415977	0.815514
H	-4.946465	-0.415977	-0.815512
Be	1.412861	0.021733	-0.000001
I	-0.762956	0.033036	-0.000005
At	3.701043	0.009848	0.000004

I–Be–At···NH_3

N	-4.504755	0.055529	-0.000024
H	-4.874993	0.999895	0.000045
H	-4.884094	-0.412956	0.815775
H	-4.884399	-0.412957	-0.815681
Be	1.400437	0.017412	-0.000035
At	-0.885736	0.032042	-0.000264
I	3.585121	0.003429	0.000182