Supporting Information

Computational details

The first important issue we have encountered to accomplish our calculations has been the choice of the computational method. We decided to focus on the Density Functional Theory (DFT) approach as implemented in two quantum chemistry packages: ADF2009 and GAMESS-US . They have been chosen for their flexibility to describe the chemical bond using several decomposition schemes, like the Extended Transition State (ETS) and the Natural Energy Decomposition Analysis (NEDA) based on the Natural Bond Orbitals (NBO) method[59-62]. Moreover, we decided to run additional MP2 calculations to assess the differences between the two approaches, in particular with respect to the total interaction energies.

We have performed all geometry optimizations using the Density Functional Theory (DFT) as implemented in ADF2009, employing the PBE correlation-exchange (xc) functional. An all-electron triple-zeta basis-set with two polarization functions, TZ2P, has been used for all atoms. All structures includes iodine, thus all calculations have been treated at the scalar relativistic ZORA approximation level of theory. Dispersion corrections by Grimme named DFT-D3[68], have also been added. No symmetry constrains were employed.

Frequency calculations were carried to assess that a minimum was found on each of the optimized structures. Pilot calculations to compute zero-point energy corrections were also carried out. However due to the weakness of the halogen bond, such corrections to the interaction energy fall within 0.1 kcal/mol, hence are negligible and not affect the overall discussion.

To describe the several facets of the halogen bond we decided to use mostly the NEDA scheme and the Extended Transition State method as they outline the bond in terms of several chemical meaningful contributions.

The NEDA calculations have been carried out with the GAMESS-US suite of programs. . A triple zeta basis set has been employed on all the atoms using the so-called def2-TZVPP library. Scalar relativistic effects have been incorporated on the iodine atom using an effective core potential (ECP) with 28 core electrons.

The NEDA scheme allows the partition of the total interaction energy between two monomers A and B to form AB, in three main terms: Electrical (EL), which includes all the Columbic-type of interactions; the core term (CORE), which raises as a consequence of the Pauli exclusion principle; the Charge Transfer term (CT), which corresponds to the electron transfer, upon bond formation, from one fragment to the other.

$$\Delta E = EL + EX + CT$$

The electrical term itself can be decomposed in three contributions: static electrostatic interaction between the unperturbed monomers (ES); induced polarization (POL) and Self-Energy (SE), which is the penalty energy needed to perturb the electron density of the two monomers once the polarization occurs.

$$EL = ES + POL + SE$$

The CORE term includes the steric exchange (EX), i.e. the Pauli repulsion between the filled orbitals of the two monomers; the deformation density (DEF), i.e. the deformation energy computed from the fully relaxed wavefunction of each monomer in the absence of the other to the orthogonalized monomers at the equilibrium position. This deformation density includes also the penalty energy SE, due to polarization effects, and must be excluded from the definition of the CORE term:

$$CORE = EX + DEF - SE$$

In conclusion the Total Interaction energy between the two monomers can be finally expressed as:

$$\Delta E = ES + POL + SE + EX + DEF - SE + CT$$

The ETS method allows choosing two molecular moieties, which in our case are the halogen donor and the acceptor. At the equilibrium, the total bonding energy is expressed as the sum between two terms:

$$\Delta E = \Delta E_{prep} + \Delta E_{int}$$

The first contribution, ΔE_{prep}, is the preparation energy and corresponds to the energy required to deform the separated fragments from their equilibrium geometry to the one they assume in the supermolecule. This term is always positive, although in some cases it can also be negligibly small. In this work we are not interested in this term for two main reasons: the deformation is small and the solvent, which undoubtedly reduces the total bond energy, is not included.

The second term is a stabilizing term called interaction energy, ΔE_{int}, which includes the instantaneous interaction between the two fragments. The ΔE_{int} term itself can be decomposed into three quantities that have a direct physical meaning:

$$\Delta E_{int} = \Delta E_{pauli} + \Delta E_{elstat} + \Delta E_{orb}$$

The first term, ΔE_{pauli}, is computed by orthonormalizing and antisymmetrizing the fragment spin-orbitals of one moiety with the fragment spin-orbitals of the second moiety at the supermolecule equilibrium position. This step ensures that same spin electrons do not occupy the same region of space. Usually this term is responsible for the increase in kinetic energy upon formation of a chemical bond and is always positive. The second term, ΔE_{elstat}, is computed as the electrostatic interaction between the unperturbed fragments at the equilibrium position. The last term, ΔE_{orb}, is computed by relaxing the orthonormalized density to the full optimized electron density of the entire supermolecule. This contribution includes the charge transfer between the occupied orbitals of one fragment and the unoccupied orbitals of the other fragment. It also includes charge transfer within the occupied and unoccupied orbitals of the same fragment, the so-called intrafragment polarization.

The intermolecular charge transfer was also computed by means of the Natural Bond Orbital (NBO) analysis and the amount of charge transferred was deduced using the Natural Population Analysis .[59-62]

The sigma-hole density plots of CF_3I and CI_3I in Figure 1 have been generated with the ADF-GUI using an iso-density surface of 0.001. The plots that include the effect of the -1.0 point charge (at the position of the chloride ion) have been computed by adding the potential exerted by the point charge in the Kohn-Sham Hamiltonian and successively fully relax the new electron density.

The same approach has been used to compute the $V_{S,max}$ for all the CY_3I monomers. In presence of the point charge, we have used a -1.0 charge when the Lewis base is a chloride ion, while for the ammonia, we have used 4 point charges (one on each atomic center) with effective charge computed at the NPA level of theory.

The MP2 calculations[74], using the Turbomole 6.0 code[75], has been used to compute the interaction energies and compare them against the DFT ones. A triple zeta basis set has been employed on all the atoms using the so-called def2-TZVPP library. Scalar relativistic effects have been incorporated on the iodine atom using an effective core potential (ECP) with 28 core electrons. In the MP2 step, the set of valence and core-valence occupied orbitals have been correlated in all virtual space. All structures have been re-optimized at this level of theory.

Geometries computed with DFT/PBE/TZ2P

CF_3I

1.c	0.000000	0.000000	1.210810
2.f	-0.631597	1.093958	1.677786
3.f	-0.631597	-1.093958	1.677786
4.f	1.263194	0.000000	1.677786
5.i	0.000000	0.000000	-0.973211

CF_3I---Cl

1.c	0.000000	0.000000	1.249303
2.f	-0.635064	1.099963	1.793980
3.f	-0.635064	-1.099963	1.793980
4.f	1.270128	0.000000	1.793980
5.i	0.000000	0.000000	-1.023346
6.cl	0.000000	0.000000	-3.793001

CF_3I---NH_3

1.C	0.000000	0.000000	1.399697
2.F	-0.633184	1.096707	1.889538

3.F	-0.633184	-1.096707	1.889538
4.F	1.266368	0.000000	1.889538
5.I	0.000000	0.000000	-0.800971
6.N	0.000000	0.000000	-3.679566
7.H	-0.952011	0.000000	-4.048349
8.H	0.476005	0.824465	-4.048349
9.H	0.476005	-0.824465	-4.048349

CF_3I---NMe_3

1.C	0.000000	0.000000	1.372596
2.I	0.000000	0.000000	-0.846158
3.F	-0.633495	1.097245	1.867557
4.F	-0.633495	-1.097245	1.867557
5.F	1.266989	0.000000	1.867557
6.N	0.000000	0.000000	-3.615902
7.C	-1.396307	0.000000	-4.061495
8.C	0.698154	1.209238	-4.061495
9.C	0.698154	-1.209238	-4.061495
10.H	0.737832	-1.277963	-5.167877
11.H	1.724864	-1.207314	-3.673374
12.H	0.183132	-2.097433	-3.673374
13.H	0.737832	1.277963	-5.167877

14.H	0.183132	2.097433	-3.673374
15.H	1.724864	1.207314	-3.673374
16.H	-1.475664	0.000000	-5.167877
17.H	-1.907996	-0.890120	-3.673374
18.H	-1.907996	0.890120	-3.673374

CCl_3I

1.c	0.000000	0.000000	1.062730
2.cl	-0.841261	1.457107	1.650532
3.cl	-0.841261	-1.457107	1.650532
4.cl	1.682522	0.000000	1.650532
5.i	0.000000	0.000000	-1.145263

CCl_3I---Cl

1.c	0.000000	0.000000	1.103378
2.cl	-0.846603	1.466360	1.772730
3.cl	-0.846603	-1.466360	1.772730
4.cl	1.693206	0.000000	1.772730
5.i	0.000000	0.000000	-1.213289
6.cl	0.000000	0.000000	-3.906027

CCl_3I---NH_3

1.C	0.000000	0.000000	1.252121
2.Cl	-0.842894	1.459934	1.858230

3.Cl	-0.842894	-1.459934	1.858230
4.Cl	1.685787	0.000000	1.858230
5.I	0.000000	0.000000	-0.978891
6.N	0.000000	0.000000	-3.765902
7.H	-0.954507	0.000000	-4.125792
8.H	0.477253	0.826627	-4.125792
9.H	0.477253	-0.826627	-4.125792

CCl_3I---NMe_3

1.C	0.000000	0.000000	1.247017
2.Cl	-0.843873	1.461631	1.854614
3.Cl	-0.843873	-1.461631	1.854614
4.Cl	1.687746	0.000000	1.854614
5.I	0.000000	0.000000	-1.001197
6.N	0.000000	0.000000	-3.666310
7.C	-1.400029	0.000000	-4.104785
8.C	0.700014	1.212461	-4.104785
9.C	0.700014	-1.212461	-4.104785
10.H	0.740517	-1.282613	-5.209477
11.H	1.724272	-1.206994	-3.711626
12.H	0.183151	-2.096761	-3.711626
13.H	0.740517	1.282613	-5.209477

14.H	0.183151	2.096761	-3.711626
15.H	1.724272	1.206994	-3.711626
16.H	-1.481034	0.000000	-5.209477
17.H	-1.907424	-0.889767	-3.711626
18.H	-1.907424	0.889767	-3.711626

CBr_3I

1.c	0.000000	0.000000	0.828432
2.br	-0.924477	1.601241	1.484539
3.br	-0.924477	-1.601241	1.484539
4.br	1.848954	0.000000	1.484539
5.i	0.000000	0.000000	-1.359125

CBr_3I---Cl

1.c	0.000000	0.000000	0.845150
2.br	-0.931473	1.613359	1.587185
3.br	-0.931473	-1.613359	1.587185
4.br	1.862947	0.000000	1.587185
5.i	0.000000	0.000000	-1.453973
6.cl	0.000000	0.000000	-4.128840

CBr_3I---NH_3

1.C	0.000000	0.000000	1.011568

2.Br	-0.925620	1.603221	1.685860
3.Br	-0.925620	-1.603221	1.685860
4.Br	1.851240	0.000000	1.685860
5.I	0.000000	0.000000	-1.202859
6.N	0.000000	0.000000	-3.987413
7.H	-0.954526	0.000000	-4.347344
8.H	0.477263	0.826644	-4.347344
9.H	0.477263	-0.826644	-4.347344

CBr_3I---NMe_3

1.C	0.000000	0.000000	1.201321
2.Br	-0.926627	1.604964	1.881342
3.Br	-0.926627	-1.604964	1.881342
4.Br	1.853253	0.000000	1.881342
5.I	0.000000	0.000000	-1.030483
6.N	0.000000	0.000000	-3.699922
7.C	-1.399727	0.000000	-4.139953
8.C	0.699863	1.212199	-4.139953
9.C	0.699863	-1.212199	-4.139953
10.H	0.739363	-1.280615	-5.244868
11.H	1.724467	-1.207129	-3.747889
12.H	0.183171	-2.096997	-3.747889

13.H	0.739363	1.280615	-5.244868
14.H	0.183171	2.096997	-3.747889
15.H	1.724467	1.207129	-3.747889
16.H	-1.478727	0.000000	-5.244868
17.H	-1.907638	-0.889867	-3.747889
18.H	-1.907638	0.889867	-3.747889

CI_3I

1.c	0.000000	0.000000	0.674109
2.i	-1.030262	1.784466	1.404601
3.i	-1.030262	-1.784466	1.404601
4.i	2.060524	0.000000	1.404601
5.i	0.000000	0.000000	-1.512233

CI_3I---Cl

1.c	0.000000	0.000000	0.679035
2.i	-1.037760	1.797453	1.489909
3.i	-1.037760	-1.797453	1.489909
4.i	2.075520	0.000000	1.489909
5.i	0.000000	0.000000	-1.628045
6.cl	0.000000	0.000000	-4.282526

CI_3I---NH_3

1.C	0.000000	0.000000	0.854796
2.I	-1.031404	1.786444	1.598352
3.I	-1.031404	-1.786444	1.598352
4.I	2.062808	0.000000	1.598352
5.I	0.000000	0.000000	-1.360786
6.N	0.000000	0.000000	-4.152255
7.H	-0.954475	0.000000	-4.512763
8.H	0.477238	0.826600	-4.512763
9.H	0.477238	-0.826600	-4.512763

CI_3I---NMe_3

1.C	0.000000	0.000000	1.153034
2.I	-1.031927	1.787350	1.896803
3.I	-1.031927	-1.787350	1.896803
4.I	2.063854	0.000000	1.896803
5.I	0.000000	0.000000	-1.083030
6.N	0.000000	0.000000	-3.743075
7.C	-1.400582	0.000000	-4.181751
8.C	0.700291	1.212940	-4.181751
9.C	0.700291	-1.212940	-4.181751
10.H	0.739482	-1.280821	-5.286576
11.H	1.724703	-1.207267	-3.789428

12.H	0.183172	-2.097270	-3.789428
13.H	0.739482	1.280821	-5.286576
14.H	0.183172	2.097270	-3.789428
15.H	1.724703	1.207267	-3.789428
16.H	-1.478965	0.000000	-5.286576
17.H	-1.907875	-0.890003	-3.789428
18.H	-1.907875	0.890003	-3.789428

ETS and NEDA

$CY_3I{-}{-}{-}Cl^-$

$CY_3I{-}{-}{-}Cl^-$	Y=F	Y=Cl	Y=Br	Y=I
ETS				
ΔE_{elstat}	-46.5	-52.5	-54.3	-55.5
ΔE_{orb}	-41.2	-54.3	-58.2	-63.6
Dispersion Energy	-0.1	-0.2	-0.2	-0.3
Total Attractive Energy	-87.8	-107.0	-112.7	-119.4
ΔE_{Pauli}	51.7	65.9	69.6	75.0
ΔE_{int}	-36.1	-41.1	-43.1	-44.4
NEDA				
ES	-47.5	-52.4	-54.2	-55.1
POL	-39.8	-48.3	-49.9	-51.0
XC	-19.8	-22.8	-23.3	-24.2
CT	-64.5	-85.1	-89.8	-95.6
DEF(A)	64.8	80.5	82.1	84.5
DEF(B)	71.8	87.8	92.5	97.4
SE(A)	20.4	24.5	25.2	26.0
SE(B)	-0.8	-0.6	-0.4	-0.6
Elec(ES+POL+SE)	-67.7	-76.7	-79.4	-80.6
Charge Tra (CT)	-64.5	-85.1	-89.8	-95.6
Core (DEF+XC-SE)	97.3	121.5	126.5	132.3
ΔE_{int}	-34.9	-40.2	-42.7	-43.9
ΔE_{int} (MP2)	-30.6	-34.0	-36.0	-37.1
VS,max	28.5	27.4	20.6	25.5
NPA Charge Transfer	0.29	0.37	0.40	0.43
Distance I--Cl	2.77	2.69	2.67	2.65

CY_3I---NH_3

CY_3I---NH_3	Y=F	Y=Cl	Y=Br	Y=I
ETS				
ΔE_{elstat}	-16.0	-20.0	-20.1	-19.6
ΔE_{orb}	-9.5	-13.2	-13.5	-13.4
Dispersion Energy	-0.7	-0.8	-0.8	-0.8
Total Attractive Energy	-26.23	-34.0	-34.4	-33.9
ΔE_{Pauli}	18.5	24.9	25.0	24.7
ΔE_{int}	-7.8	-9.1	-9.4	-9.2
NEDA				
ES	-15.3	-18.9	-19.1	-18.6
POL	-18.2	-22.1	-22.4	-22.3
XC	-11.0	-13.2	-13.3	-13.2
CT	-18.2	-24.9	-25.1	-24.6
DEF(A)	28.5	35.6	35.0	34.0
DEF(B)	27.1	35.0	36.1	36.2
SE(A)	6.9	8.3	8.2	8.0
SE(B)	2.2	2.7	3.1	3.2
Elec(ES+POL+SE)	-24.5	-29.9	-30.3	-29.7
Charge Tra (CT)	-18.2	-24.9	-25.1	-24.6
Core (DEF+XC-SE)	-35.6	46.4	46.6	45.7
ΔE_{int}	-7.2	-8.5	-8.8	-8.6
ΔE_{int} (MP2)	-5.5	-6.0	-6.3	-6.2
VS,max	28.5	27.4	20.6	25.5
NPA Charge Transfer	0.08	0.11	0.12	0.12
Distance I--N	2.88	2.79	2.78	2.79

CY_3I---NMe_3

CY_3I---NH_3	Y=F	Y=Cl	Y=Br	Y=I
ETS				
ΔE_{elstat}	-23.2	-30.7	-30.4	-31.3
ΔE_{orb}	-14.9	-21.0	-21.3	-22.0
Dispersion Energy	-2.1	-2.3	-2.4	-2.5
Total Attractive Energy	-40.2	-54.0	-54.1	-55.8
ΔE_{Pauli}	28.8	40.6	39.9	41.6
ΔE_{int}	-11.4	-13.5	-14.2	-14.2
NEDA				
ES	-20.9	-27.4	-27.1	-27.9
POL	-14.6	-19.1	-19.5	-20.3
XC	-12.6	-15.7	-15.5	-16.1
CT	-27.5	-37.9	-38.1	-39.4
DEF(A)	41.2	55.6	54.7	56.8
DEF(B)	25.6	34.2	34.6	35.9
SE(A)	7.6	10.0	10.0	10.4
SE(B)	-0.2	-0.2	-0.01	-0.02
Elec(ES+POL+SE)	-28.1	-36.7	-36.6	-37.7
Charge Tra (CT)	-27.5	-37.9	-38.1	-39.4
Core (DEF+XC-SE)	47.1	64.3	63.8	66.2
ΔE_{int}	*-8.5*	*-10.3*	*-10.9*	*-10.9*
ΔE_{int} (MP2)	*-11.0*	*-13.4*	*-14.2*	*-14.6*
NPA Charge Transfer	0.10	0.15	0.16	0.17
Distance I--N	2.77	2.66	2.67	2.66

Table 1: Interaction energy between the CY_3X [Y=I, Br, Cl] and the X = [Cl^-, Br^-, I^-, NH_3]. All calculations have been performed at DFT/PBE/TZ2P level of theory. Energies are in kcal/mol, distances in Å.

Total Bond Energy	Y=F	Y=Cl	Y=Br	Y=I
CY_3I---F^-	*-62.2*	*-66.8*	*-69.5*	*-70.4*
CY_3I---Cl^-	*-36.1*	*-41.1*	*-43.1*	*-44.3*
CY_3I---Br^-	*-31.9*	*-36.9*	*-39.0*	*-40.4*
CY_3I---I^-	-27.5	*-32.8*	*-35.2*	*-36.6*
CY_3I---NH_3	*-7.8*	*-9.1*	*-9.4*	*-9.2*
Total Bond Energy	*Y=F*	*Y=Cl*	*Y=Br*	*Y=I*
CY_3Br---F^-	*-48.8*	*-54.1*	*-56.7*	*-57.5*
CY_3Br---Cl^-	*-26.2*	*-31.4*	*-33.6*	*-34.9*
CY_3Br---Br^-	*-22.6*	*-27.9*	*-30.1*	*-31.6*
CY_3Br---I^-	*-18.8*	*-24.6*	*-27.0*	*-28.5*
CY_3Br---NH_3	*-5.4*	*-6.3*	*-6.6*	*-6.3*
Total Bond Energy	*Y=F*	*Y=Cl*	*Y=Br*	*Y=I*
CY_3Cl---F^-	*-35.7*	*-42.2*	*-45.2*	*-46.8*
CY_3Cl---Cl^-	*-16.4*	*-21.3*	*-24.0*	*-26.0*
CY_3Cl---Br^-	*-13.5*	*-18.1*	*-20.8*	*-23.0*
CY_3Cl---I^-	*-10.4*	*-14.8*	*-17.5*	*-20.1*
CY_3Cl---NH_3	*-3.2*	*-3.5*	*-3.7*	*-3.5*