Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

On the directionality of halogen bonding

Stefan M. Huber, Joseph D. Scanlon, Elisa Jimenez-Izal, Jesus M. Ugalde, and Ivan Infante

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 (linear)

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---Cl (perpendicular)

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	-2.769655	0.000000	-1.023346

CF_3I---NH_3 (linear)

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---NH_3 (perpendicular)

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	1.439295	-2.492933	-0.805995
7.H	0.909263	-3.223821	-1.282643
8.H	2.337279	-2.399356	-1.282643
9.H	1.624517	-2.813747	0.145370

C_6F_5I---Cl (linear)

1.C	0.000000	0.000000	-0.015404
2.C	-1.186996	0.000000	0.712965
3.C	-1.208455	0.000000	2.110279
4.C	0.000000	0.000000	2.813102
5.C	1.208455	0.000000	2.110279
6.C	1.186996	0.000000	0.712965
7.F	-2.393855	0.000000	0.077240
8.F	-2.382360	0.000000	2.803887
9.F	0.000000	0.000000	4.173249
10.F	2.382360	0.000000	2.803887
11.F	2.393855	0.000000	0.077240
12.I	0.000000	0.000000	-2.263106

13.Cl	0.000000	0.000000	-4.988729

C_6F_5I---Cl (perpendicular)

1.C	0.000000	0.000000	-0.015404
2.C	-1.186996	0.000000	0.712965
3.C	-1.208455	0.000000	2.110279
4.C	0.000000	0.000000	2.813102
5.C	1.208455	0.000000	2.110279
6.C	1.186996	0.000000	0.712965
7.F	-2.393855	0.000000	0.077240
8.F	-2.382360	0.000000	2.803887
9.F	0.000000	0.000000	4.173249
10.F	2.382360	0.000000	2.803887
11.F	2.393855	0.000000	0.077240
12.I	0.000000	0.000000	-2.263106
13.Cl	0.000000	2.725623	-2.263106

C_6F_5I---NH_3 (linear)

1.C	-0.657036	0.000318	1.199072
2.C	0.061995	0.000154	0.000000
3.C	-0.657036	0.000318	-1.199072

4.C	-2.054916	-0.000294	-1.210711
5.C	-2.755266	-0.001877	0.000000
6.C	-2.054916	-0.000294	1.210711
7.I	2.188709	0.002915	0.000000
8.F	-0.015102	0.000858	-2.390286
9.F	-2.733763	-0.000217	-2.377918
10.F	-4.102783	-0.005996	0.000000
11.F	-2.733763	-0.000217	2.377918
12.F	-0.015102	0.000858	2.390286
13.N	5.066113	-0.014738	0.000000
14.H	5.430162	-0.968596	0.000000
15.H	5.441670	0.457527	0.823580
16.H	5.441670	0.457527	-0.823580

C_6F_5I---NH_3 (perpendicular)

1.C	-0.657036	0.000318	1.199072
2.C	0.061995	0.000154	0.000000
3.C	-0.657036	0.000318	-1.199072
4.C	-2.054916	-0.000294	-1.210711
5.C	-2.755266	-0.001877	0.000000
6.C	-2.054916	-0.000294	1.210711

7.F	-0.015102	0.000858	-2.390286
8.F	-2.733763	-0.000217	-2.377918
9.F	-4.102783	-0.005996	0.000000
10.F	-2.733763	-0.000217	2.377918
11.F	-0.015102	0.000858	2.390286
12.I	2.188709	0.002915	0.000000
13.N	2.192445	-2.874540	0.000000
14.H	1.241319	-3.245670	0.000000
15.H	2.667488	-3.246577	0.823580
16.H	2.667488	-3.246577	-0.823580

I_2---Cl (linear)

1.I	0.000000	0.000000	-0.548847
2.I	0.000000	0.000000	2.409894
3.Cl	0.000000	0.000000	5.030084

I_2---Cl (perpendicular)

1.I	0.000000	0.000000	-0.548847
2.I	0.000000	0.000000	2.409894
3.Cl	2.620190	0.000000	2.409894

I_2---NH_3 (linear)

1.I	0.000000	0.000000	-0.708619
2.I	0.000000	0.000000	-3.474335
3.N	0.000000	0.000000	1.962705
4.H	-0.958429	0.000000	2.309809
5.H	0.479215	0.830024	2.309809
6.H	0.479215	-0.830024	2.309809

I_2---NH_3 (perpendicular)

1.I	0.000000	0.000000	-0.708619
2.I	0.000000	0.000000	-3.474335
3.N	-2.671320	0.000000	-0.703957
4.H	-3.020096	0.000000	-1.661778
5.H	-3.017587	0.830024	-0.224137
6.H	-3.017587	-0.830024	-0.224137

Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Bond Decomposition using the Ziegler-Rauk scheme as implemented in the ADF package.

Linear

Complex	CF_3I—Cl^-	CF_3I—NH_3	TFBzI—Cl^-	TFBzI—NH_3	I_2—Cl^-	I_2—NH_3
ΔE_{elstat}	-46.5	-16.0	-49.2	-15.8	-62.1	-26.9
ΔE_{orb}	-41.2	-9.5	-48.4	-9.4	-69.5	-19.9
Disp.	-0.1	-0.7	-0.2	-0.8	-0.1	-0.8
Total Attr. En.	-87.8	-26.2	-97.8	-26.0	-131.7	-47.6
ΔE_{pauli}	51.7	18.5	58.4	18.0	79.6	34.8
ΔE_{int}	-36.1	-7.8	-39.3	-8.0	-52.2	-12.7
NPA charge	0.26	0.08	0.29	0.08	0.39	0.14
Distance	2.77	2.88	2.73	2.88	2.62	2.67

Perpendicular

Complex	CF_3I—Cl^-	CF_3I—NH_3	TFBzI—Cl^-	TFBzI—NH_3	I_2—Cl^-	I_2—NH_3
ΔE_{elstat}	-48.4	-15.8	-54.4	-15.4	-69.3	-29.2
ΔE_{orb}	-27.1	-5.0	-32.9	-5.2	-50.7	-8.9
Disp.	-0.5	-1.1	-0.7	-1.3	-0.4	-1.2
Total Attr. En.	-75.9	-21.9	-88.0	-21.9	-120.4	-39.3
ΔE_{pauli}	79.4	30.7	89.6	30.2	123.1	57.2
ΔE_{int}	3.5	8.7	1.6	8.3	2.7	17.9
NPA charge	0.21	0.03	0.25	0.03	0.22	0.04
Distance	2.77	2.88	2.73	2.88	2.62	2.67

Linear

Complex	CF_3Br—Cl^-	CF_3Br—NH_3	TFBzBr—Cl^-	TFBzBr—NH_3	Br_2—Cl^-	Br_2—NH_3
ΔE_{elstat}	-32.1	-10.0	-34.6	-9.7	-58.4	-29.0
ΔE_{orb}	-31.7	-6.0	-40.2	-5.9	-76.8	-25.4
Disp.	-0.2	-0.7	-0.2	-0.7	-0.2	-0.8
Total Attr. En.	-64.0	-16.7	-75.0	-16.3	-135.4	-55.2
ΔE_{pauli}	37.9	11.3	45.3	10.8	81.8	40.5
ΔE_{int}	-26.2	-5.4	-29.7	-5.5	-53.6	-14.7
NPA charge	0.21	0.05	0.26	0.05	0.41	0.17
Distance	2.72	2.87	2.66	2.88	2.46	2.47

Perpendicular

Complex	CF_3Br—Cl^-	CF_3Br—NH_3	TFBzBr—Cl^-	TFBzBr—NH_3	Br_2—Cl^-	Br_2—NH_3
ΔE_{elstat}	-33.7	-9.3	-39.6	-8.7	-4.8	-31.7
ΔE_{orb}	-17.3	-2.8	-23.0	-2.9	-27.1	-8.5
Disp.	-0.6	-1.1	-0.9	-1.3	-0.4	-1.2
Total Attr. En.	-51.6	-13.2	-63.5	-12.9	-32.3	-41.4
ΔE_{pauli}	57.4	18.5	67.8	17.6	3.9	65.1
ΔE_{int}	5.9	5.3	4.3	4.7	-28.5	23.8
NPA charge	0.11	0.01	0.16	0.02	0.36	0.03
Distance	2.72	2.87	2.66	2.88	2.46	2.47

Linear

Complex	CF_3Cl—Cl^-	CF_3Cl—NH_3	TFBzCl—Cl^-	TFBzCl—NH_3	Cl_2—Cl^-	Cl_2—NH_3
ΔE_{elstat}	-19.5	-5.0	-19.4	-4.7	-54.8	-24.4
ΔE_{orb}	-19.3	-2.6	-26.4	-2.7	-85.1	-24.2
Disp.	-0.2	-0.6	-0.3	-0.7	-0.2	-0.7
Total Attr. En.	-39.0	-8.2	-46.1	-8.1	-140.1	-49.3
ΔE_{pauli}	22.6	5.0	27.6	5.1	87.2	37.2
ΔE_{int}	-16.4	-3.2	-18.5	-3.0	-52.9	-12.1
NPA charge	0.14	0.02	0.19	0.02	0.43	0.16
Distance	2.79	3.01	2.73	3.00	2.34	2.40

Perpendicular

Complex	CF_3Cl—Cl^-	CF_3Cl—NH_3	TFBzCl—Cl^-	TFBzCl—NH_3	Cl_2—Cl^-	Cl_2—NH_3
ΔE_{elstat}	-20.6	-4.5	-23.9	-3.9	-64.6	-26.7
ΔE_{orb}	-10.5	-1.3	-15.4	-1.4	-34.4	-7.3
Disp.	-0.6	-1.1	-1.0	-1.3	-0.3	-1.1
Total Attr. En.	-31.7	-6.9	-40.3	-6.6	-99.3	-35.1
ΔE_{pauli}	34.5	8.3	40.0	7.9	130.0	57.7
ΔE_{int}	2.8	1.4	-0.3	1.4	30.7	22.4
NPA charge	0.06	0.01	0.11	0.01	0.15	0.01
Distance	2.79	3.01	2.73	3.00	2.34	2.40

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