Supplementary Information

Halogen bonds with carbenes acting as Lewis base units: complexes of imidazol-2-ylidene: theoretical analysis and experimental evidences

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Complexes of imidazol-2-ylidene ($C_3N_2H_4$)

ωB97XD/aug-cc-pVTZ results (ωB97XD/aug-cc-pVTZ-PP for iodine)

$C_3N_2H_4 + I_2$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	0.180024	-0.000384	-0.000032
2	7	0	3.329133	-1.055852	0.000032
3	7	0	3.328152	1.055997	0.000038
4	6	0	2.504872	-0.000314	0.000018
5	6	0	4.655275	0.674148	0.000004
6	6	0	4.655908	-0.672757	0.000015
7	1	0	2.990249	2.002173	0.000057
8	1	0	2.992146	-2.002349	0.000044
9	1	0	5.466093	1.377917	-0.000010
10	1	0	5.467376	-1.375776	0.000011
11	53	0	-2.716122	0.000206	0.000017

$C_3N_2H_4 + Br_2$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	-0.200697	-0.000001	0.000004
2	7	0	2.583294	1.061309	-0.000119
3	7	0	2.583269	-1.061299	0.000071
4	6	0	1.772942	0.000014	0.000014
5	6	0	3.909037	-0.673470	-0.000147
6	6	0	3.909052	0.673449	0.000176
7	1	0	2.238294	-2.005769	0.000114
8	1	0	2.238345	2.005788	-0.000216
9	1	0	4.720029	-1.376820	-0.000256
10	1	0	4.720060	1.376779	0.000303
11	35	0	-2.874414	0.000001	-0.000001

$C_3N_2H_4 + Cl_2$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	-0.879415	-0.000360	-0.000050
2	7	0	1.644065	-1.066382	0.000097
3	7	0	1.643727	1.066428	-0.000023
4	6	0	0.841685	-0.000104	-0.000048
5	6	0	2.968611	0.673449	0.000089
6	6	0	2.968817	-0.673000	-0.000091
7	1	0	1.293589	2.009627	0.000046
8	1	0	1.294222	-2.009691	0.000180
9	1	0	3.779542	1.376676	0.000147
10	1	0	3.779963	-1.375981	-0.000171

11	17	0	-3.463911	0.000182	0.000026

$C_3N_2H_4 + F_2$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	9	0	-1.558707	-0.000089	-0.955853
2	7	0	0.301018	-1.114706	-0.161567
3	7	0	0.300977	1.114612	-0.161710
4	6	0	-0.554060	-0.000009	-0.042133
5	6	0	1.624236	0.664955	0.006729
6	6	0	1.624350	-0.664881	0.006405
7	1	0	-0.009657	1.963709	0.277243
8	1	0	-0.009369	-1.963317	0.278563
9	1	0	2.449162	1.352800	0.012944
10	1	0	2.449370	-1.352619	0.012315
11	9	0	-1.248028	0.000055	1.162061

$C_3N_2H_4 + HCCI$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.141195	-0.000101	-0.000153
2	6	0	-4.342502	-0.000389	-0.000369
3	1	0	-5.404905	-0.001089	-0.000520
4	53	0	-1.096879	0.000141	0.000127
5	7	0	2.609568	-1.048086	-0.000020
6	7	0	2.609974	1.048053	-0.000143
7	6	0	1.758330	0.000146	-0.000180
8	6	0	3.940242	0.672668	0.000050

9	6	0	3.939982	-0.673221	-0.000160
10	1	0	2.285033	1.996728	-0.000170
11	1	0	2.284252	-1.996628	0.000050
12	1	0	4.752397	1.375285	0.000161
13	1	0	4.751863	-1.376155	-0.000200

$C_3N_2H_4$ + HCCBr

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.241090	0.014904	0.000007
2	6	0	-4.438690	0.037393	0.000013
3	1	0	-5.500104	0.057171	0.000017
4	35	0	-1.432134	-0.018477	-0.000003
5	7	0	2.457515	-1.051287	-0.000007
6	7	0	2.389274	1.040366	-0.000008
7	6	0	1.565338	-0.033462	-0.000022
8	6	0	3.732191	0.710451	0.000015
9	6	0	3.776097	-0.634460	0.000016
10	1	0	2.035774	1.978283	-0.000016
11	1	0	2.166141	-2.010264	-0.000013
12	1	0	4.521259	1.439137	0.000028
13	1	0	4.611006	-1.310124	0.000030

$C_3N_2H_4$ + HCCCl

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.585218	0.003363	0.004263
2	6	0	-4.781223	0.017652	0.012313

3	1	0	-5.842174	0.030379	0.018983
4	17	0	-1.941087	-0.015995	-0.006259
5	7	0	2.052630	1.041272	-0.005840
6	7	0	2.091033	-1.049685	-0.005142
7	6	0	1.209894	-0.019991	-0.016689
8	6	0	3.415849	-0.652306	0.011882
9	6	0	3.391086	0.692962	0.011446
10	1	0	1.787047	-2.004525	-0.009042
11	1	0	1.713715	1.984300	-0.010336
12	1	0	4.241266	-1.339575	0.022606
13	1	0	4.190653	1.410150	0.021767

$C_3N_2H_4$ + HCCF

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.691653	0.077215	-0.000000
2	6	0	-2.688965	1.268653	0.000081
3	1	0	-2.721110	2.328669	0.000159
4	9	0	-2.730858	-1.185431	-0.000092
5	7	0	0.684416	0.565318	-0.000001
6	7	0	2.004170	-1.056949	0.000063
7	6	0	0.673597	-0.789400	0.000086
8	6	0	2.802295	0.072961	-0.000034
9	6	0	1.951897	1.116374	-0.000075
10	1	0	2.354047	-1.995672	0.000114
11	1	0	-0.174373	1.086923	-0.000011
12	1	0	3.876104	0.041504	-0.000065
13	1	0	2.139922	2.174052	-0.000148

$C_3N_2H_4$ + ICN

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.126009	0.001219	0.000160
2	7	0	-4.277675	0.002696	0.000168
3	53	0	-1.032278	-0.000885	-0.000083
4	7	0	2.470592	-1.050029	0.000116
5	7	0	2.467837	1.050092	0.000143
6	6	0	1.625995	-0.001084	0.000134
7	6	0	3.797470	0.674859	-0.000067
8	6	0	3.799247	-0.671225	-0.000023
9	1	0	2.140160	1.998427	0.000228
10	1	0	2.145483	-1.999242	0.000180
11	1	0	4.607988	1.379195	-0.000166
12	1	0	4.611622	-1.373413	-0.000076

$C_3N_2H_4$ + BrCN

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.194742	0.000204	0.000004
2	7	0	4.345030	0.000491	0.000032
3	35	0	1.372343	-0.000230	-0.000008
4	7	0	-2.309607	-1.047409	-0.000003
5	7	0	-2.308768	1.047271	-0.000012
6	6	0	-1.454871	-0.000412	-0.000024
7	6	0	-3.639691	0.673257	0.000023
8	6	0	-3.640234	-0.672321	0.000017
9	1	0	-1.986436	1.996606	-0.000009

10	1	0	-1.988042	-1.997003	-0.000038
11	1	0	-4.451342	1.376528	0.000034
12	1	0	-4.452449	-1.374939	0.000046

$C_3N_2H_4$ + ClCN

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.516073	-0.005004	-0.003534
2	7	0	4.665784	-0.021980	-0.008355
3	17	0	1.873865	0.018551	0.003908
4	7	0	-2.002931	1.052283	0.003538
5	7	0	-1.949999	-1.039225	0.004117
6	6	0	-1.116867	0.028313	0.011317
7	6	0	-3.290440	-0.699703	-0.007514
8	6	0	-3.324510	0.645295	-0.007897
9	1	0	-1.605744	-1.980480	0.007415
10	1	0	-1.706636	2.009701	0.006267
11	1	0	-4.084594	-1.422802	-0.014382
12	1	0	-4.154238	1.327267	-0.015068

$C_3N_2H_4$ + FCN

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.393583	0.168309	-0.000038
2	7	0	2.253470	1.308905	-0.000015
3	9	0	2.689436	-1.050368	0.000014
4	7	0	-0.715282	0.770633	0.000015
5	7	0	-1.572518	-1.139939	0.000031

6	6	0	-0.360517	-0.533286	0.000015
7	6	0	-2.634036	-0.253536	-0.000077
8	6	0	-2.080033	0.974037	0.000059
9	1	0	-1.668194	-2.137203	-0.000011
10	1	0	-0.014168	1.493549	0.000035
11	1	0	-3.663200	-0.561317	-0.000081
12	1	0	-2.533037	1.947951	-0.000036

ωB97XD/aug-cc-pVDZ results (ωB97XD/aug-cc-pVDZ-PP for iodine)

$C_3N_2H_4 + I_2$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	-0.192768	0.000768	-0.000077
2	7	0	-3.336658	1.061066	0.000226
3	7	0	-3.334289	-1.061205	0.000189
4	6	0	-2.507783	0.000868	0.000155
5	6	0	-4.666077	-0.679551	-0.000069
6	6	0	-4.667603	0.676403	-0.000149
7	1	0	-2.991866	-2.011146	0.000233
8	1	0	-2.996477	2.011743	0.000388
9	1	0	-5.482579	-1.389464	-0.000171
10	1	0	-5.485635	1.384423	-0.000360
11	53	0	2.734315	-0.000407	0.000028

$C_3N_2H_4 + Br_2$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	-0.193968	0.000225	0.000308

2	7	0	2.589886	-1.066425	0.000111
3	7	0	2.590372	1.066395	0.000087
4	6	0	1.775918	0.000170	0.000437
5	6	0	3.920548	0.677678	-0.000442
6	6	0	3.920237	-0.678312	-0.000511
7	1	0	2.241811	2.014821	0.000254
8	1	0	2.240873	-2.014688	0.000385
9	1	0	4.737898	1.386340	-0.000812
10	1	0	4.737230	-1.387303	-0.000923
11	35	0	-2.889456	-0.000116	-0.000228

$C_3N_2H_4 + Cl_2$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	-0.882560	-0.001032	-0.000963
2	7	0	1.655386	-1.071102	0.000073
3	7	0	1.654531	1.071123	0.000112
4	6	0	0.849730	-0.000289	0.000177
5	6	0	2.984147	0.678386	0.000215
6	6	0	2.984653	-0.677197	0.000258
7	1	0	1.300049	2.018416	0.000275
8	1	0	1.301905	-2.018389	0.000267
9	1	0	3.801425	1.387831	0.000657
10	1	0	3.801760	-1.385238	0.000769
11	17	0	-3.487189	0.000553	0.000541

$C_3N_2H_4 + F_2$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	9	0	-1.571165	0.000797	-0.956602
2	7	0	0.301626	-1.118479	-0.168611
3	7	0	0.301683	1.118514	-0.167075
4	6	0	-0.550362	0.000059	-0.044442
5	6	0	1.629531	0.669560	0.007748
6	6	0	1.629605	-0.669488	0.007217
7	1	0	-0.014464	1.966263	0.282287
8	1	0	-0.014210	-1.965769	0.281883
9	1	0	2.460416	1.363346	0.012327
10	1	0	2.460533	-1.363253	0.010756
11	9	0	-1.247511	-0.000978	1.172091

$C_3N_2H_4$ + HCCI

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.147456	0.000147	0.000066
2	6	0	-4.361514	0.000280	-0.000032
3	1	0	-5.432037	0.000526	-0.000085
4	53	0	-1.089941	-0.000104	0.000147
5	7	0	2.603528	-1.052760	0.000033
6	7	0	2.603317	1.052814	-0.000226
7	6	0	1.746876	-0.000061	0.000034
8	6	0	3.938301	0.677653	-0.000388
9	6	0	3.938438	-0.677331	-0.000529
10	1	0	2.274738	2.005615	-0.000215
11	1	0	2.275140	-2.005628	0.000264
12	1	0	4.756481	1.386131	-0.000543
13	1	0	4.756759	-1.385644	-0.000760

$C_3N_2H_4$ + HCCBr

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.238836	-0.000291	0.000012
2	6	0	-4.449062	-0.000672	-0.000409
3	1	0	-5.518475	-0.001106	-0.000734
4	35	0	-1.421591	0.000337	0.000549
5	7	0	2.413441	-1.051094	-0.000235
6	7	0	2.414024	1.051044	-0.000307
7	6	0	1.549781	0.000215	0.000089
8	6	0	3.749983	0.676957	-0.000922
9	6	0	3.749607	-0.677747	-0.000779
10	1	0	2.088573	2.004429	-0.000191
11	1	0	2.087461	-2.004298	-0.000048
12	1	0	4.568899	1.384774	-0.001336
13	1	0	4.568128	-1.386020	-0.001065

$C_3N_2H_4$ + HCCCl

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.585144	0.000000	0.000130
2	6	0	4.793486	0.000389	0.000229
3	1	0	5.862360	0.000555	0.000362
4	17	0	1.929115	-0.000288	-0.000151
5	7	0	-2.067545	-1.050133	-0.000068
6	7	0	-2.067688	1.050304	-0.000047
7	6	0	-1.199642	0.000150	-0.000337
8	6	0	-3.404350	0.677266	0.000174

9	6	0	-3.404257	-0.677294	0.000208
10	1	0	-1.743307	2.003820	-0.000068
11	1	0	-1.743027	-2.003601	-0.000098
12	1	0	-4.223422	1.385070	0.000347
13	1	0	-4.223226	-1.385218	0.000403

$C_3N_2H_4$ + HCCF

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.981984	-0.000012	-0.000151
2	6	0	5.184140	0.000127	0.000004
3	1	0	6.252714	0.000212	0.000485
4	9	0	2.706400	-0.000150	-0.000506
5	7	0	-1.975507	-1.049517	-0.000039
6	7	0	-1.975721	1.049623	-0.000040
7	6	0	-1.104287	0.000142	-0.000478
8	6	0	-3.312996	0.677156	0.000584
9	6	0	-3.312858	-0.677322	0.000553
10	1	0	-1.651634	2.003040	-0.000178
11	1	0	-1.651226	-2.002867	-0.000180
12	1	0	-4.132518	1.384665	0.000984
13	1	0	-4.132235	-1.384998	0.000927

$C_3N_2H_4$ + HCCF second local minimum

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.671916	0.076306	0.000064
2	6	0	-2.669860	1.279906	-0.000018

3	1	0	-2.708834	2.348094	-0.000085
4	9	0	-2.718009	-1.193422	0.000112
5	7	0	0.687999	0.596757	-0.000023
6	7	0	1.964130	-1.071345	-0.000043
7	6	0	0.634795	-0.763881	-0.000025
8	6	0	2.799477	0.037063	-0.000045
9	6	0	1.974913	1.112499	-0.000029
10	1	0	2.286065	-2.025367	-0.000054
11	1	0	-0.161134	1.143094	-0.000013
12	1	0	3.880358	-0.026592	-0.000057
13	1	0	2.196270	2.172322	-0.000025

$C_3N_2H_4$ + ICN

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.136117	0.000039	0.000184
2	7	0	-4.298976	0.000010	0.000143
3	53	0	-1.028021	-0.000010	0.000086
4	7	0	2.467665	-1.054936	-0.000163
5	7	0	2.467611	1.054929	-0.000057
6	6	0	1.619666	-0.000027	0.000019
7	6	0	3.801354	0.677607	-0.000293
8	6	0	3.801390	-0.677549	-0.000405
9	1	0	2.137561	2.007802	0.000059
10	1	0	2.137661	-2.007825	-0.000132
11	1	0	4.618992	1.386472	-0.000386
12	1	0	4.619064	-1.386374	-0.000595

$C_3N_2H_4$ + BrCN

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.195569	-0.000022	-0.000005
2	7	0	4.356880	-0.000053	0.000027
3	35	0	1.365349	0.000025	-0.000008
4	7	0	-2.303715	-1.052006	0.000002
5	7	0	-2.303814	1.052023	0.000002
6	6	0	-1.444083	0.000050	-0.000000
7	6	0	-3.639172	0.677269	0.000005
8	6	0	-3.639108	-0.677378	0.000005
9	1	0	-1.978691	2.005790	0.000002
10	1	0	-1.978501	-2.005742	0.000002
11	1	0	-4.457426	1.385691	0.000007
12	1	0	-4.457295	-1.385877	0.000007

$C_3N_2H_4$ + ClCN

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.521617	-0.000064	-0.000013
2	7	0	4.682310	-0.000177	0.000058
3	17	0	1.867591	0.000164	-0.000021
4	7	0	-1.976121	-1.050614	-0.000006
5	7	0	-1.976718	1.050779	-0.000006
6	6	0	-1.110752	0.000332	-0.000048
7	6	0	-3.312824	0.676923	0.000025
8	6	0	-3.312438	-0.677523	0.000028
9	1	0	-1.653821	2.004954	-0.000016
10	1	0	-1.652677	-2.004604	-0.000023

11	1	0	-4.131622	1.384901	0.000057
12	1	0	-4.130831	-1.385970	0.000061

$C_3N_2H_4$ + FCN

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.707242	0.000031	-0.000132
2	7	0	4.865493	0.000040	-0.000512
3	9	0	2.444432	-0.000064	0.000273
4	7	0	-1.772463	-1.049650	-0.000131
5	7	0	-1.772738	1.049762	-0.000076
6	6	0	-0.901978	0.000171	-0.000292
7	6	0	-3.109769	0.677050	0.000335
8	6	0	-3.109591	-0.677289	0.000398
9	1	0	-1.450041	2.003689	-0.000206
10	1	0	-1.449516	-2.003492	-0.000300
11	1	0	-3.929082	1.384698	0.000563
12	1	0	-3.928718	-1.385153	0.000668