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

ELECTRONIC SUPPLEMENTARY INFORMATION

Rethinking the X^- + CH_3Y [X = OH, SH, CN, NH_2, PH_2; Y = F, Cl, Br, I] S_N2 reactions

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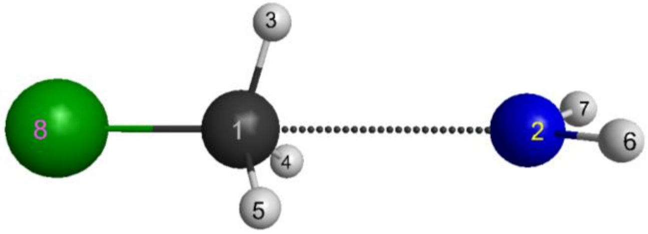
Content

Table S1. Energies, structures, and frequencies for the PreMIN [Y = F, Cl, Br] ion-dipole complexes (C_s symmetry) obtained at different levels of theory

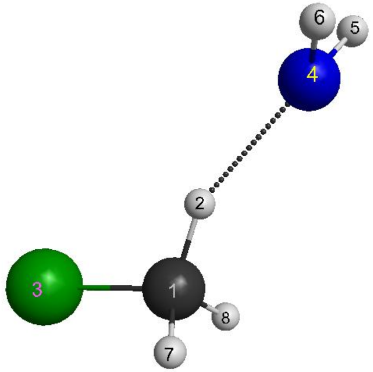


1	C						
2	N	1	r_1				
3	H	1	r_2	2	a_1		
4	H	1	r_3	2	a_2	3	d_1
5	H	1	r_3	2	a_2	3	$-d_1$
6	H	2	r_4	1	a_3	3	d_2
7	H	2	r_4	1	a_3	3	$-d_2$
8	Y	1	r_5	3	a_4	2	180.0

Level[a]	**MP2/aug-cc-pVDZ**			**CCSD(T)-F12b/aug-cc-pVDZ**		**CCSD(T)-F12b/aug-cc-pVTZ**	
System	**$FCH_3\cdots NH_2^-$**	**$ClCH_3\cdots NH_2^-$**	**$BrCH_3\cdots NH_2^-$**	**$FCH_3\cdots NH_2^-$**	**$ClCH_3\cdots NH_2^-$**	**$FCH_3\cdots NH_2^-$**	**$ClCH_3\cdots NH_2^-$**
Energy [E_h]	−195.194146	−555.205059	−511.169956	−195.436811	−555.417945	−195.471860	−555.462948
r_1 [Å]	2.833	2.759	2.663	2.844	2.802	2.841	2.777
r_2 [Å]	1.092	1.090	1.089	1.085	1.082	1.083	1.080
r_3 [Å]	1.093	1.091	1.090	1.086	1.083	1.084	1.081
r_4 [Å]	1.036	1.036	1.035	1.028	1.028	1.027	1.027
r_5 [Å]	1.453	1.859	2.050	1.423	1.829	1.424	1.839
a_1 [deg]	71.8	72.0	66.4	68.3	60.7	68.1	64.0
a_2 [deg]	71.6	72.5	78.1	72.4	77.1	72.5	75.9
a_3 [deg]	129.0	128.7	120.3	129.0	128.0	129.0	128.1
a_4 [deg]	108.5	107.9	106.5	109.4	109.5	109.3	109.0
d_1 [deg]	120.3	120.4	121.8	121.0	122.6	121.0	122.0
d_2 [deg]	108.5	85.0	115.8	91.9	99.2	91.9	98.5
ZPE [cm^{-1}]	13026	12655	12489	12974	12580	12979	12607
ω_1 [cm^{-1}]	20i	28i	50i	2i	43i	37i	32i
ω_2 [cm^{-1}]	64	58	67	69	55	57	62
ω_3 [cm^{-1}]	85	80	88	71	68	75	71
ω_4 [cm^{-1}]	163	156	127	158	148	157	148
ω_5 [cm^{-1}]	167	167	186	166	160	163	160
ω_6 [cm^{-1}]	197	172	223	184	167	188	169
ω_7 [cm^{-1}]	891	584	407	941	596	935	593
ω_8 [cm^{-1}]	1119	969	894	1133	953	1130	955
ω_9 [cm^{-1}]	1124	978	914	1143	992	1142	982
ω_{10} [cm^{-1}]	1379	1262	1168	1399	1286	1401	1286
ω_{11} [cm^{-1}]	1462	1432	1418	1479	1452	1483	1461
ω_{12} [cm^{-1}]	1467	1439	1424	1486	1465	1491	1471
ω_{13} [cm^{-1}]	1468	1465	1461	1503	1499	1507	1503
ω_{14} [cm^{-1}]	3142	3160	3165	3098	3121	3101	3130
ω_{15} [cm^{-1}]	3267	3296	3316	3198	3233	3202	3246
ω_{16} [cm^{-1}]	3279	3306	3327	3213	3246	3217	3257
ω_{17} [cm^{-1}]	3335	3338	3340	3314	3317	3314	3318
ω_{18} [cm^{-1}]	3442	3448	3452	3395	3401	3395	3401

[a] For Br effective core potential and the corresponding aug-cc-pVDZ-PP basis set are employed.

Table S2. Energies, structures, and frequencies for the HMIN [Y = Cl, Br, I] H-bonded complexes (C_s symmetry) obtained at different levels of theory

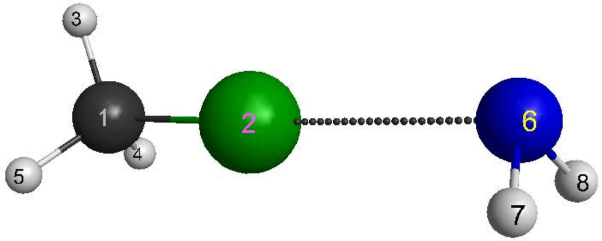


1	C						
2	H	1	r_1				
3	Y	1	r_2	2	a_1		
4	N	2	r_3	1	a_2	3	180.0
5	H	4	r_4	2	a_3	1	d_1
6	H	4	r_4	2	a_3	1	$-d_1$
7	H	1	r_5	3	a_4	2	d_2
8	H	1	r_5	3	a_4	2	$-d_2$

Level[a]	MP2/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVTZ		
System	$ClCH_2H\cdots NH_2^-$	$BrCH_2H\cdots NH_2^-$	$ICH_2H\cdots NH_2^-$	$ClCH_2H\cdots NH_2^-$	$BrCH_2H\cdots NH_2^-$	$ICH_2H\cdots NH_2^-$	$ClCH_2H\cdots NH_2^-$	$BrCH_2H\cdots NH_2^-$	$ICH_2H\cdots NH_2^-$
Energy [E_h]	−555.205422	−511.170457	−390.316815	−555.418682	−511.380069	−390.521703	−555.463380	−511.427267	−390.559794
r_1 [Å]	1.120	1.126	1.140	1.110	1.115	1.130	1.108	1.113	1.127
r_2 [Å]	1.830	1.980	2.181	1.804	1.971	2.167	1.813	1.974	2.168
r_3 [Å]	1.936	1.888	1.817	1.950	1.901	1.834	1.958	1.910	1.841
r_4 [Å]	1.035	1.034	1.034	1.027	1.026	1.026	1.026	1.025	1.025
r_5 [Å]	1.098	1.098	1.099	1.089	1.088	1.089	1.087	1.086	1.087
a_1 [deg]	111.4	111.0	110.1	111.7	110.9	109.8	111.6	110.8	109.6
a_2 [deg]	157.6	159.6	163.3	157.4	158.8	163.8	155.8	157.9	163.4
a_3 [deg]	127.5	127.0	122.8	127.0	126.3	120.8	127.2	126.7	121.9
a_4 [deg]	106.2	105.6	105.3	106.8	105.6	105.3	106.5	105.5	105.1
d_1 [deg]	100.6	102.0	111.6	102.5	104.3	114.5	101.4	102.8	112.9
d_2 [deg]	121.3	121.5	121.7	121.2	121.4	121.6	121.2	121.3	121.5
ZPE [cm^{-1}]	12694	12523	12338	12712	12533	12283	12674	10538	12359
ω_1 [cm^{-1}]	70	68	47	72	75	44*i*	68	60	56
ω_2 [cm^{-1}]	76	71	64	112	95	67	71	94	69
ω_3 [cm^{-1}]	92	97	124	123	113	108	91	112	140
ω_4 [cm^{-1}]	178	152	155	182	166	161	175	158	167
ω_5 [cm^{-1}]	211	217	229	215	223	230	211	221	233
ω_6 [cm^{-1}]	294	308	334	287	301	324	274	293	325
ω_7 [cm^{-1}]	671	569	512	672	564	504	672	561	503
ω_8 [cm^{-1}]	1001	953	917	1018	958	924	1008	958	924
ω_9 [cm^{-1}]	1050	992	937	1061	991	932	1051	992	933
ω_{10} [cm^{-1}]	1368	1333	1306	1389	1345	1319	1387	1346	1320
ω_{11} [cm^{-1}]	1448	1439	1428	1465	1457	1446	1471	1462	1452
ω_{12} [cm^{-1}]	1470	1468	1468	1504	1501	1502	1507	1505	1505
ω_{13} [cm^{-1}]	1522	1520	1523	1542	1535	1538	1540	1538	1540
ω_{14} [cm^{-1}]	2799	2710	2492	2792	2712	2492	2812	2734	2519
ω_{15} [cm^{-1}]	3134	3133	3120	3095	3105	3094	3105	3112	3100
ω_{16} [cm^{-1}]	3199	3202	3194	3148	3166	3162	3160	3174	3168
ω_{17} [cm^{-1}]	3347	3351	3356	3331	3336	3338	3329	3335	3339
ω_{18} [cm^{-1}]	3459	3465	3470	3415	3422	3426	3415	3421	3426

[a] For Br and I effective core potentials and the corresponding aug-cc-pVDZ-PP and aug-cc-pVTZ-PP basis sets are employed.

Table S3. Energies, structures, and frequencies for the FSMIN [Y = Cl, Br, I] front-side complexes (C_s symmetry) obtained at different levels of theory

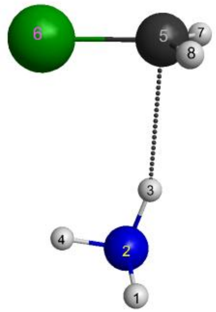


1	C						
2	Y	1	r_1				
3	H	1	r_2	2	a_1		
4	H	1	r_3	2	a_2	3	d_1
5	H	1	r_3	2	a_2	3	$-d_1$
6	N	2	r_4	1	a_3	3	0.0
7	H	6	r_5	2	a_4	3	d_2
8	H	6	r_5	2	a_4	3	$-d_2$

Level[a]	**MP2/aug-cc-pVDZ**			**CCSD(T)-F12b/aug-cc-pVDZ**			**CCSD(T)-F12b/aug-cc-pVTZ**		
System	**$CH_3Cl\cdots NH_2^-$**	**$CH_3Br\cdots NH_2^-$**	**$CH_3I\cdots NH_2^-$**	**$CH_3Cl\cdots NH_2^-$**	**$CH_3Br\cdots NH_2^-$**	**$CH_3I\cdots NH_2^-$**	**$CH_3Cl\cdots NH_2^-$**	**$CH_3Br\cdots NH_2^-$**	**$CH_3I\cdots NH_2^-$**
Energy [E_h]	−555.182982	−511.165771	−390.331342	−555.398808	−511.375592	−390.536491	−555.443150	−511.422802	−390.574684
r_1 [Å]	1.824	2.132	2.341	1.805	2.094	2.317	1.821	2.091	2.315
r_2 [Å]	1.100	1.103	1.103	1.092	1.092	1.094	1.090	1.090	1.092
r_3 [Å]	1.100	1.102	1.103	1.092	1.092	1.094	1.090	1.090	1.092
r_4 [Å]	2.773	2.398	2.463	2.736	2.422	2.437	2.681	2.425	2.438
r_5 [Å]	1.037	1.035	1.034	1.029	1.026	1.024	1.028	1.025	1.024
a_1 [deg]	109.3	108.5	109.1	109.5	108.7	109.3	109.3	108.6	109.1
a_2 [deg]	109.4	108.5	109.0	109.7	108.7	109.2	109.4	108.6	109.0
a_3 [deg]	176.1	178.7	178.5	177.2	179.0	178.8	178.0	179.0	178.8
a_4 [deg]	109.1	99.5	102.0	101.8	99.0	102.2	101.5	99.0	102.1
d_1 [deg]	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0
d_2 [deg]	124.7	128.0	127.2	127.4	128.0	127.0	127.5	127.9	126.9
ZPE [cm^{-1}]	12618	12613	12614	12630	12594	12582	12608	12610	12587
ω_1 [cm^{-1}]	17*i*	11*i*	27	88*i*	55*i*	8*i*	9	86*i*	78*i*
ω_2 [cm^{-1}]	80	146	136	96	150	139	101	154	148
ω_3 [cm^{-1}]	102	150	140	128	152	143	109	156	149
ω_4 [cm^{-1}]	126	238	288	131	225	276	135	225	275
ω_5 [cm^{-1}]	232	374	371	279	396	379	268	399	380
ω_6 [cm^{-1}]	240	577	603	303	541	596	282	535	591
ω_7 [cm^{-1}]	655	580	617	624	546	614	618	537	607
ω_8 [cm^{-1}]	976	761	708	993	784	712	969	786	709
ω_9 [cm^{-1}]	977	767	725	995	789	728	970	792	726
ω_{10} [cm^{-1}]	1313	1120	1101	1331	1168	1126	1324	1169	1123
ω_{11} [cm^{-1}]	1453	1436	1434	1479	1458	1455	1487	1463	1457
ω_{12} [cm^{-1}]	1465	1437	1435	1480	1459	1455	1488	1465	1459
ω_{13} [cm^{-1}]	1466	1478	1486	1490	1513	1522	1497	1514	1522
ω_{14} [cm^{-1}]	3057	3032	3028	3025	3013	3003	3029	3017	3005
ω_{15} [cm^{-1}]	3163	3154	3146	3111	3114	3102	3118	3120	3105
ω_{16} [cm^{-1}]	3164	3155	3147	3111	3115	3103	3119	3120	3106
ω_{17} [cm^{-1}]	3326	3354	3360	3299	3338	3361	3304	3338	3360
ω_{18} [cm^{-1}]	3440	3468	3474	3386	3426	3451	3390	3427	3451

[a] For Br and I effective core potentials and the corresponding aug-cc-pVDZ-PP and aug-cc-pVTZ-PP basis sets are employed.

Table S4. Energies, structures, and frequencies for the DITS [Y = F, Cl, Br, I] double-inversion transition states (C_1 symmetry) obtained at different levels of theory

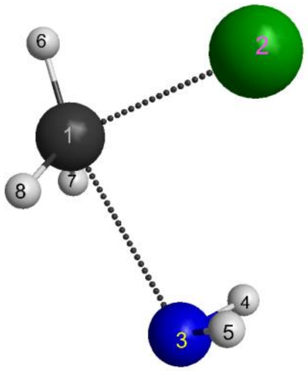


1	H						
2	N	1	r_1				
3	H	2	r_2	1	a_1		
4	H	2	r_3	3	a_2	1	d_1
5	C	3	r_4	2	a_3	1	d_2
6	Y	5	r_5	3	a_4	2	d_3
7	H	5	r_6	6	a_5	2	d_4
8	H	5	r_7	6	a_6	2	d_5

Level[a]	MP2/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVTZ			
System	$[H_2NH\cdots CH_2F]^-$	$[H_2NH\cdots CH_2Cl]^-$	$[H_2NH\cdots CH_2Br]^-$	$[H_2NH\cdots CH_2I]^-$	$[H_2NH\cdots CH_2F]^-$	$[H_2NH\cdots CH_2Cl]^-$	$[H_2NH\cdots CH_2Br]^-$	$[H_2NH\cdots CH_2I]^-$	$[H_2NH\cdots CH_2F]^-$	$[H_2NH\cdots CH_2Cl]^-$	$[H_2NH\cdots CH_2Br]^-$	$[H_2NH\cdots CH_2I]^-$
Energy [E_h]	−195.154806	−555.183791	−511.152363	−390.304547	−195.401002	−555.401389	−511.365616	−390.513706	−195.435904	−555.445948	−511.412793	−390.552163
r_1 [Å]	1.023	1.023	1.023	1.023	1.016	1.016	1.016	1.016	1.015	1.015	1.015	1.015
r_2 [Å]	1.041	1.043	1.043	1.042	1.033	1.034	1.034	1.033	1.032	1.034	1.033	1.032
r_3 [Å]	1.023	1.023	1.023	1.023	1.016	1.016	1.016	1.016	1.016	1.015	1.015	1.015
r_4 [Å]	2.301	2.294	2.304	2.323	2.330	2.321	2.332	2.352	2.330	2.319	2.334	2.359
r_5 [Å]	1.450	1.802	1.937	2.114	1.425	1.775	1.930	2.097	1.426	1.783	1.932	2.098
r_6 [Å]	1.087	1.086	1.087	1.088	1.078	1.077	1.076	1.077	1.076	1.075	1.075	1.075
r_7 [Å]	1.087	1.086	1.087	1.088	1.078	1.077	1.077	1.077	1.076	1.075	1.075	1.076
a_1 [deg]	102.9	104.3	104.3	104.4	102.8	104.5	104.5	104.6	102.8	104.5	104.5	104.6
a_2 [deg]	104.2	103.4	103.6	103.9	104.4	103.3	103.6	103.9	104.5	103.4	103.5	103.8
a_3 [deg]	202.8	166.6	169.1	172.2	207.3	163.0	166.3	169.4	207.0	163.9	166.2	169.0
a_4 [deg]	75.8	84.7	86.9	90.2	76.1	84.9	87.3	90.6	75.9	85.1	87.2	90.6
a_5 [deg]	114.5	115.6	115.6	116.1	114.8	116.0	115.5	116.2	114.8	115.9	115.4	116.1
a_6 [deg]	114.4	115.6	115.6	116.1	114.7	116.0	115.5	116.2	114.7	115.9	115.4	116.1
d_1 [deg]	109.3	109.4	109.4	109.5	109.5	109.7	109.7	109.8	109.6	109.6	109.6	109.7
d_2 [deg]	178.8	262.3	267.2	274.7	176.0	264.3	270.3	279.0	176.3	265.9	270.7	278.9
d_3 [deg]	11.4	−16.8	−18.3	−20.1	11.4	−17.1	−18.7	−21.9	11.9	−17.5	−18.4	−20.9
d_4 [deg]	91.4	84.2	84.3	84.2	91.2	85.2	85.5	85.6	91.1	85.4	85.6	85.7
d_5 [deg]	276.5	270.7	270.7	270.7	275.7	271.4	271.1	271.5	275.5	271.0	270.9	271.3
ZPE [cm^{-1}]	12972	12804	12714	12637	12942	12768	12675	12621	12940	12750	12647	12600
ω_1 [cm^{-1}]	952i	862i	865i	841i	960i	851i	888i	853i	967i	875i	902i	864i
ω_2 [cm^{-1}]	99	86	72	61	94	77	54	47	90	79	68	53
ω_3 [cm^{-1}]	101	95	89	80	99	101	98	105	98	93	81	92
ω_4 [cm^{-1}]	151	160	158	153	151	150	160	156	147	156	152	153
ω_5 [cm^{-1}]	158	168	167	165	158	158	165	170	155	158	155	162
ω_6 [cm^{-1}]	295	320	319	315	281	299	302	304	280	295	293	298
ω_7 [cm^{-1}]	376	400	405	404	362	388	398	393	361	386	387	386
ω_8 [cm^{-1}]	913	710	619	576	934	704	601	562	928	699	596	559
ω_9 [cm^{-1}]	1070	954	905	852	1081	966	901	847	1081	954	894	841
ω_{10} [cm^{-1}]	1189	1193	1192	1186	1205	1207	1208	1201	1207	1209	1207	1202
ω_{11} [cm^{-1}]	1393	1354	1332	1313	1397	1362	1317	1300	1397	1344	1307	1290
ω_{12} [cm^{-1}]	1625	1628	1630	1632	1650	1655	1657	1660	1655	1658	1661	1664
ω_{13} [cm^{-1}]	1663	1672	1673	1675	1685	1697	1699	1700	1690	1700	1701	1703
ω_{14} [cm^{-1}]	3198	3167	3171	3187	3169	3174	3177	3171	3172	3177	3179	3173
ω_{15} [cm^{-1}]	3211	3212	3209	3201	3225	3206	3211	3230	3225	3200	3209	3231
ω_{16} [cm^{-1}]	3395	3382	3382	3370	3340	3330	3345	3334	3343	3336	3348	3336
ω_{17} [cm^{-1}]	3509	3509	3509	3510	3490	3493	3494	3496	3489	3492	3492	3495
ω_{18} [cm^{-1}]	3597	3596	3596	3595	3564	3566	3565	3566	3564	3565	3564	3565

[a] For Br and I effective core potentials and the corresponding aug-cc-pVDZ-PP and aug-cc-pVTZ-PP basis sets are employed.

Table S5. Energies, structures, and frequencies for the FSTS [Y = F, Cl, Br, I] front-side attack transition states (C_s symmetry) obtained at different levels of theory

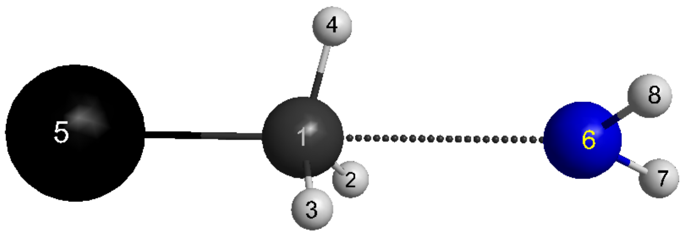


1	C					
2	Y	1	r_1			
3	N	1	r_2	2	a_1	
4	H	3	r_3	1	a_2	2	d_1
5	H	3	r_3	1	a_2	2	$-d_1$
6	H	1	r_4	2	a_3	3	180.0
7	H	1	r_5	3	a_4	2	d_2
8	H	1	r_5	3	a_4	2	$-d_2$

Level[a]	MP2/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVTZ			
System	$[H_2N\cdots CH_3\cdots F]^-$	$[H_2N\cdots CH_3\cdots Cl]^-$	$[H_2N\cdots CH_3\cdots Br]^-$	$[H_2N\cdots CH_3\cdots I]^-$	$[H_2N\cdots CH_3\cdots F]^-$	$[H_2N\cdots CH_3\cdots Cl]^-$	$[H_2N\cdots CH_3\cdots Br]^-$	$[H_2N\cdots CH_3\cdots I]^-$	$[H_2N\cdots CH_3\cdots F]^-$	$[H_2N\cdots CH_3\cdots Cl]^-$	$[H_2N\cdots CH_3\cdots Br]^-$	$[H_2N\cdots CH_3\cdots I]^-$
Energy [E_h]	−195.125918	−555.148462	−511.119619	−390.270534	−195.364914	−555.365229	−511.335042	−390.482482	−195.400155	−555.409382	−511.381518	−390.519450
r_1 [Å]	1.745	2.161	2.289	2.471	1.779	2.227	2.342	2.487	1.781	2.226	2.347	2.504
r_2 [Å]	2.096	2.293	2.336	2.388	2.130	2.555	2.628	2.707	2.136	2.483	2.558	2.638
r_3 [Å]	1.034	1.035	1.035	1.035	1.025	1.026	1.027	1.027	1.024	1.025	1.026	1.026
r_4 [Å]	1.117	1.104	1.104	1.103	1.101	1.084	1.084	1.083	1.099	1.083	1.083	1.082
r_5 [Å]	1.101	1.094	1.093	1.093	1.088	1.081	1.081	1.082	1.086	1.079	1.079	1.080
a_1 [deg]	81.7	85.6	86.3	87.1	80.8	83.3	84.9	86.0	80.8	84.2	85.2	86.2
a_2 [deg]	101.2	102.5	102.9	102.5	98.7	91.0	91.6	87.9	98.5	94.3	94.0	90.8
a_3 [deg]	81.3	82.6	83.0	83.8	79.9	84.2	85.3	87.4	79.8	82.5	83.7	85.5
a_4 [deg]	80.7	74.5	73.6	72.7	80.0	69.8	68.3	67.6	79.9	70.6	69.1	68.2
d_1 [deg]	308.4	307.9	307.7	307.7	309.0	309.7	309.6	309.6	309.0	309.4	309.3	309.5
d_2 [deg]	123.8	120.2	119.7	119.2	123.4	117.2	115.9	115.6	123.3	117.7	116.6	116.1
ZPE [cm^{-1}]	13031	12785	12680	12562	12919	12225	12323	12013	12946	12535	12201	11984
ω_1 [cm^{-1}]	668*i*	725*i*	694*i*	723*i*	683*i*	722*i*	821*i*	1097*i*	686*i*	701*i*	708*i*	843*i*
ω_2 [cm^{-1}]	87	106	97	95	68	90	111	17	91	174	67	46*i*
ω_3 [cm^{-1}]	272	222	186	162	229	161	150	105	231	176	138	41
ω_4 [cm^{-1}]	335	298	290	262	307	180	231	138	305	251	142	107
ω_5 [cm^{-1}]	463	383	361	340	401	191	235	178	401	261	218	194
ω_6 [cm^{-1}]	527	389	370	345	513	208	262	194	504	328	229	205
ω_7 [cm^{-1}]	732	591	552	503	716	450	442	370	715	506	434	376
ω_8 [cm^{-1}]	953	828	800	769	911	622	652	603	910	691	631	600
ω_9 [cm^{-1}]	1042	900	861	817	1001	778	767	696	998	801	744	687
ω_{10} [cm^{-1}]	1306	1232	1205	1183	1280	1082	1050	1053	1287	1125	1089	1076
ω_{11} [cm^{-1}]	1428	1397	1393	1389	1433	1404	1409	1397	1440	1417	1404	1397
ω_{12} [cm^{-1}]	1496	1471	1463	1457	1491	1425	1430	1420	1495	1444	1429	1426
ω_{13} [cm^{-1}]	1511	1496	1492	1487	1550	1525	1535	1528	1552	1540	1531	1527
ω_{14} [cm^{-1}]	2878	3019	3029	3040	2917	3086	3101	3096	2924	3087	3090	3091
ω_{15} [cm^{-1}]	3049	3153	3166	3176	3063	3207	3221	3200	3073	3209	3215	3208
ω_{16} [cm^{-1}]	3153	3248	3256	3261	3151	3259	3264	3253	3160	3266	3267	3260
ω_{17} [cm^{-1}]	3363	3365	3364	3365	3363	3354	3353	3349	3364	3359	3350	3349
ω_{18} [cm^{-1}]	3467	3473	3473	3475	3443	3428	3432	3428	3443	3436	3426	3426

[a] For Br and I effective core potentials and the corresponding aug-cc-pVDZ-PP and aug-cc-pVTZ-PP basis sets are employed.

Table S6. Energies, structures, and frequencies for the PreTS [Y = I] transition states (C_1 symmetry) obtained at different levels of theory

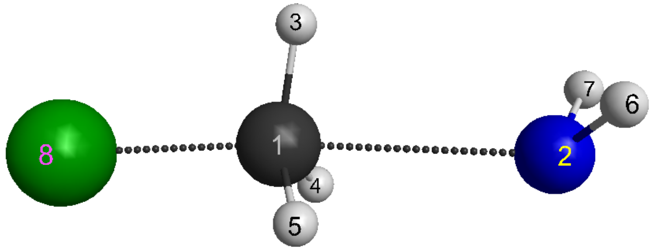


1	C						
2	H	1	r_1				
3	H	1	r_2	2	a_1		
4	H	1	r_3	2	a_2	3	d_1
5	Y	1	r_4	4	a_3	2	d_2
6	N	3	r_5	1	a_4	2	d_3
7	H	6	r_6	1	a_5	3	d_4
8	H	6	r_7	1	a_6	3	$-d_5$

Level[a]	MP2/aug-cc-pVDZ	CCSD(T)-F12b/aug-cc-pVDZ	CCSD(T)-F12b/aug-cc-pVTZ
Energy [E_h]	−390.315390	−390.520178	−390.558526
r_1 [Å]	1.090	1.080	1.078
r_2 [Å]	1.089	1.079	1.077
r_3 [Å]	1.089	1.079	1.077
r_4 [Å]	2.253	2.240	2.250
r_5 [Å]	2.521	2.513	2.511
r_6 [Å]	1.034	1.026	1.025
r_7 [Å]	1.034	1.026	1.025
a_1 [deg]	112.8	112.8	113.1
a_2 [deg]	112.6	112.5	113.0
a_3 [deg]	105.7	105.8	105.4
a_4 [deg]	82.5	83.2	82.1
a_5 [deg]	131.1	131.7	131.1
a_6 [deg]	125.8	125.1	125.5
d_1 [deg]	130.3	129.9	131.2
d_2 [deg]	−114.5	−114.6	−114.1
d_3 [deg]	66.7	66.6	67.3
d_4 [deg]	114.3	109.6	115.6
d_5 [deg]	65.7	69.6	64.1
ZPE [cm^{-1}]	12329	12306	12262
ω_1 [cm^{-1}]	246*i*	264*i*	276*i*
ω_2 [cm^{-1}]	34	60	33*i*
ω_3 [cm^{-1}]	81	92	78
ω_4 [cm^{-1}]	118	116	110
ω_5 [cm^{-1}]	145	148	139
ω_6 [cm^{-1}]	193	189	194
ω_7 [cm^{-1}]	345	330	311
ω_8 [cm^{-1}]	845	838	836
ω_9 [cm^{-1}]	861	855	853
ω_{10} [cm^{-1}]	1130	1137	1132
ω_{11} [cm^{-1}]	1410	1430	1432
ω_{12} [cm^{-1}]	1416	1438	1441
ω_{13} [cm^{-1}]	1449	1483	1485
ω_{14} [cm^{-1}]	3165	3148	3151
ω_{15} [cm^{-1}]	3318	3284	3290
ω_{16} [cm^{-1}]	3330	3296	3301
ω_{17} [cm^{-1}]	3351	3339	3340
ω_{18} [cm^{-1}]	3469	3431	3433

[a] For I effective core potentials and the corresponding aug-cc-pVDZ-PP and aug-cc-pVTZ-PP basis sets are employed.

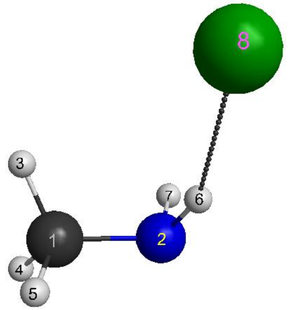
Table S7. Energies, structures, and frequencies for the WaldenTS [Y = F, Cl] transition states (C_s symmetry) obtained at different levels of theory



1	C						
2	N	1	r_1				
3	H	1	r_2	2	a_1		
4	H	1	r_3	2	a_2	3	d_1
5	H	1	r_3	2	a_2	3	$-d_1$
6	H	2	r_4	1	a_3	3	d_2
7	H	2	r_4	1	a_3	3	$-d_2$
8	Y	1	r_5	3	a_4	2	180.0

Level	MP2/aug-cc-pVDZ		CCSD(T)-F12b/aug-cc-pVDZ		CCSD(T)-F12b/aug-cc-pVTZ	
System	$[F{\cdot}CH_3{\cdot}NH_2]^-$	$[Cl{\cdot}CH_3{\cdot}NH_2]^-$	$[F{\cdot}CH_3{\cdot}NH_2]^-$	$[Cl{\cdot}CH_3{\cdot}NH_2]^-$	$[F{\cdot}CH_3{\cdot}NH_2]^-$	$[Cl{\cdot}CH_3{\cdot}NH_2]^-$
Energy [E_h]	−195.182073	−555.203107	−195.421524	−555.415425	−195.456971	−555.460749
r_1 [Å]	2.194	2.453	2.170	2.460	2.172	2.462
r_2 [Å]	1.084	1.085	1.074	1.076	1.073	1.074
r_3 [Å]	1.084	1.086	1.075	1.076	1.073	1.074
r_4 [Å]	1.035	1.035	1.027	1.028	1.026	1.027
r_5 [Å]	1.705	2.010	1.708	2.006	1.708	2.002
a_1 [deg]	87.4	82.9	87.3	81.8	87.2	81.8
a_2 [deg]	81.9	75.8	82.8	76.0	82.8	75.8
a_3 [deg]	107.7	111.8	105.6	107.5	105.5	108.1
a_4 [deg]	95.8	101.6	95.2	101.7	95.2	101.8
d_1 [deg]	120.0	119.5	120.1	119.6	120.1	119.6
d_2 [deg]	54.8	56.9	53.9	54.7	53.9	55.0
ZPE [cm^{-1}]	13220	12738	13146	12639	13147	12642
ω_1 [cm^{-1}]	561i	362i	600i	371i	598i	361i
ω_2 [cm^{-1}]	140	80	132	82	128	61
ω_3 [cm^{-1}]	238	139	246	149	247	141
ω_4 [cm^{-1}]	281	183	280	176	281	177
ω_5 [cm^{-1}]	361	266	347	261	346	261
ω_6 [cm^{-1}]	497	359	515	364	515	355
ω_7 [cm^{-1}]	544	372	558	365	555	361
ω_8 [cm^{-1}]	1080	958	1073	932	1072	939
ω_9 [cm^{-1}]	1099	965	1092	936	1091	944
ω_{10} [cm^{-1}]	1188	1128	1178	1114	1174	1123
ω_{11} [cm^{-1}]	1400	1408	1401	1419	1401	1427
ω_{12} [cm^{-1}]	1401	1413	1402	1423	1401	1431
ω_{13} [cm^{-1}]	1483	1468	1516	1503	1519	1505
ω_{14} [cm^{-1}]	3174	3191	3148	3168	3151	3170
ω_{15} [cm^{-1}]	3345	3344	3323	3318	3324	3319
ω_{16} [cm^{-1}]	3371	3368	3330	3330	3334	3331
ω_{17} [cm^{-1}]	3378	3377	3336	3334	3339	3335
ω_{18} [cm^{-1}]	3460	3457	3414	3405	3416	3406

Table S8. Energies, structures, and frequencies for the PostHMIN [Y = F, Cl, Br, I] H-bonded complexes (C_1 symmetry) obtained at different levels of theory



1	C						
2	N	1	r_1				
3	H	1	r_2	2	a_1		
4	H	1	r_3	2	a_2	3	d_1
5	H	1	r_4	2	a_3	3	d_2
6	H	2	r_5	1	a_4	3	d_3
7	H	2	r_6	1	a_5	3	d_4
8	Y	6	r_7	2	a_6	7	d_5

Level[a]	**MP2/aug-cc-pVDZ**				**CCSD(T)-F12b/aug-cc-pVDZ**				**CCSD(T)-F12b/aug-cc-pVTZ**			
System	**$CH_3NH_2 \cdots F^-$**	**$CH_3NH_2 \cdots Cl^-$**	**$CH_3NH_2 \cdots Br^-$**	**$CH_3NH_2 \cdots I^-$**	**$CH_3NH_2 \cdots F^-$**	**$CH_3NH_2 \cdots Cl^-$**	**$CH_3NH_2 \cdots Br^-$**	**$CH_3NH_2 \cdots I^-$**	**$CH_3NH_2 \cdots F^-$**	**$CH_3NH_2 \cdots Cl^-$**	**$CH_3NH_2 \cdots Br^-$**	**$CH_3NH_2 \cdots I^-$**
Energy [E_h]	−195.267900	−555.312607	−511.284597	−390.437401	−195.506945	−555.523934	−511.495079	−390.643393	−195.541935	−555.568939	−511.542224	−390.681558
r_1 [Å]	1.466	1.472	1.473	1.474	1.458	1.463	1.464	1.464	1.458	1.464	1.465	1.465
r_2 [Å]	1.111	1.106	1.106	1.106	1.103	1.098	1.098	1.097	1.101	1.096	1.096	1.096
r_3 [Å]	1.107	1.104	1.104	1.103	1.099	1.096	1.096	1.095	1.097	1.094	1.094	1.093
r_4 [Å]	1.103	1.101	1.101	1.101	1.094	1.093	1.093	1.093	1.093	1.091	1.091	1.091
r_5 [Å]	1.068	1.034	1.031	1.029	1.061	1.026	1.024	1.021	1.060	1.026	1.023	1.021
r_6 [Å]	1.023	1.022	1.022	1.022	1.016	1.015	1.015	1.015	1.015	1.014	1.014	1.014
r_7 [Å]	1.589	2.345	2.540	2.805	1.577	2.331	2.542	2.816	1.579	2.330	2.539	2.826
a_1 [deg]	114.7	114.1	114.1	114.0	114.4	113.9	113.9	113.9	114.4	113.8	113.9	113.9
a_2 [deg]	111.3	110.1	109.8	109.7	111.4	110.2	109.9	109.8	111.3	110.1	110.0	109.8
a_3 [deg]	108.6	108.7	108.7	108.8	108.8	108.9	108.9	108.9	108.8	108.9	108.9	108.9
a_4 [deg]	106.7	106.1	106.2	106.5	106.6	106.4	106.6	106.9	106.7	106.3	106.6	107.0
a_5 [deg]	107.9	108.0	108.1	108.0	108.0	108.2	108.3	108.4	107.9	108.1	108.2	108.3
a_6 [deg]	187.6	201.0	203.9	207.0	188.7	201.4	204.3	207.4	188.3	201.0	203.8	207.4
d_1 [deg]	122.9	122.8	122.8	122.5	122.8	122.7	122.7	122.5	122.7	122.6	122.6	122.5
d_2 [deg]	−119.3	−119.6	−119.6	−120.0	−119.1	−119.5	−119.5	−119.9	−119.2	−119.5	−119.5	−119.9
d_3 [deg]	53.2	51.2	52.2	52.0	53.3	51.4	52.7	52.2	53.3	51.3	53.5	52.2
d_4 [deg]	−58.5	−59.0	−58.3	−57.9	−58.7	−59.6	−58.7	−58.7	−58.8	−59.7	−57.6	−58.7
d_5 [deg]	−97.5	−102.6	−97.2	−115.2	−97.5	−102.7	−97.9	−114.4	−98.2	−103.5	−103.2	−114.5
ZPE [cm^{-1}]	14192	14287	14274	14266	14180	14068	14257	14214	14166	14268	14244	14227
ω_1 [cm^{-1}]	121	69	65	57	124	$179i$	58	59	119	71	64	57
ω_2 [cm^{-1}]	144	109	101	97	158	4	119	79	137	113	99	84
ω_3 [cm^{-1}]	301	165	140	122	305	149	146	120	302	171	140	121
ω_4 [cm^{-1}]	513	393	381	358	516	329	377	342	515	389	368	340
ω_5 [cm^{-1}]	978	962	954	952	984	948	958	953	982	967	958	953
ω_6 [cm^{-1}]	1055	1002	995	989	1056	988	1001	993	1054	1007	1000	993
ω_7 [cm^{-1}]	1087	1078	1076	1075	1089	1072	1077	1075	1088	1076	1073	1072
ω_8 [cm^{-1}]	1252	1214	1208	1206	1265	1209	1216	1212	1264	1224	1217	1213
ω_9 [cm^{-1}]	1416	1377	1371	1368	1433	1378	1385	1378	1432	1391	1384	1379
ω_{10} [cm^{-1}]	1421	1426	1428	1429	1437	1444	1445	1446	1438	1445	1448	1449
ω_{11} [cm^{-1}]	1479	1481	1481	1483	1489	1478	1492	1492	1492	1495	1496	1497
ω_{12} [cm^{-1}]	1504	1507	1507	1509	1515	1504	1520	1519	1519	1523	1522	1524
ω_{13} [cm^{-1}]	1703	1663	1657	1655	1726	1687	1680	1677	1726	1687	1682	1678
ω_{14} [cm^{-1}]	2757	3023	3028	3030	2766	2980	2993	2995	2766	2990	2994	2998
ω_{15} [cm^{-1}]	2981	3093	3099	3105	2946	3036	3047	3053	2946	3045	3049	3058
ω_{16} [cm^{-1}]	3045	3136	3141	3141	2995	3079	3090	3088	2997	3088	3093	3094
ω_{17} [cm^{-1}]	3112	3340	3378	3414	3062	3340	3387	3420	3064	3337	3380	3417
ω_{18} [cm^{-1}]	3514	3535	3539	3542	3491	3512	3522	3527	3492	3517	3520	3528

[a] For Br and I effective core potentials and the corresponding aug-cc-pVDZ-PP and aug-cc-pVTZ-PP basis sets are employed.