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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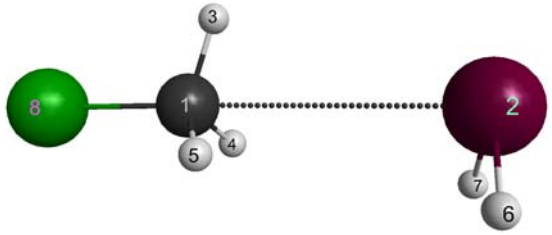
Content

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

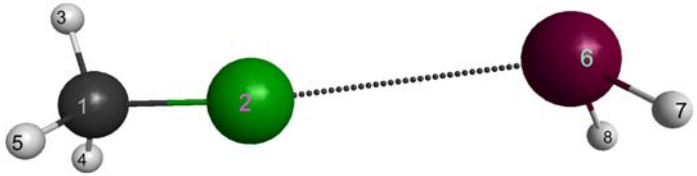


1	C						
2	P	1	r_1				
3	H	1	r_2	2	a_1		
4	H	1	r_3	2	a_2	3	d_1
5	H	1	r_3	2	a_2	3	$-d_1$
6	H	2	r_4	1	a_3	3	d_2
7	H	2	r_4	1	a_3	3	$-d_2$
8	Y	1	r_5	3	a_4	2	180.0

Level[a]	MP2/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVTZ		
System	**$FCH_3\cdots PH_2^-$**	**$ClCH_3\cdots PH_2^-$**	**$BrCH_3\cdots PH_2^-$**	**$FCH_3\cdots PH_2^-$**	**$ClCH_3\cdots PH_2^-$**	**$BrCH_3\cdots PH_2^-$**	**$FCH_3\cdots PH_2^-$**	**$ClCH_3\cdots PH_2^-$**	**$BrCH_3\cdots PH_2^-$**
Energy [E_h]	−481.457381	−841.467356	−797.432401	−481.697466	−841.677661	−797.639141	−481.738819	−841.728931	−797.692813
r_1 [Å]	3.434	3.450	3.360	3.458	3.521	3.380	3.463	3.518	3.380
r_2 [Å]	1.095	1.093	1.092	1.087	1.084	1.082	1.086	1.082	1.081
r_3 [Å]	1.095	1.093	1.092	1.088	1.084	1.083	1.086	1.082	1.081
r_4 [Å]	1.440	1.440	1.441	1.431	1.434	1.434	1.429	1.432	1.431
r_5 [Å]	1.437	1.842	2.014	1.407	1.815	2.002	1.409	1.824	2.004
a_1 [deg]	64.2	66.8	72.0	63.1	75.2	74.2	63.2	72.7	74.4
a_2 [deg]	75.3	74.5	73.2	75.0	69.4	71.9	75.1	71.1	72.1
a_3 [deg]	128.2	108.1	93.2	128.8	79.8	84.9	129.2	86.7	87.0
a_4 [deg]	108.5	108.1	107.2	109.2	108.7	107.3	109.1	108.4	107.1
d_1 [deg]	122.0	121.4	120.2	122.2	118.9	119.6	122.2	119.7	119.6
d_2 [deg]	112.9	130.5	133.7	112.1	133.2	133.8	111.2	133.9	133.9
ZPE [cm^{-1}]	11750	11343	11209	11695	11228	11129	11668	11212	11116
ω_1 [cm^{-1}]	29	30	43	41	35*i*	46	64*i*	52*i*	39*i*
ω_2 [cm^{-1}]	54	39	60	60	19	56	35	22*i*	55
ω_3 [cm^{-1}]	73	48	62	72	52	63	75	23	60
ω_4 [cm^{-1}]	97	89	85	91	84	85	91	82	82
ω_5 [cm^{-1}]	106	107	134	107	102	128	104	99	129
ω_6 [cm^{-1}]	116	117	149	110	112	138	110	105	135
ω_7 [cm^{-1}]	947	623	468	997	629	468	991	627	465
ω_8 [cm^{-1}]	1083	987	917	1086	995	916	1082	988	916
ω_9 [cm^{-1}]	1149	988	917	1169	997	917	1168	989	917
ω_{10} [cm^{-1}]	1150	1082	1081	1170	1082	1084	1169	1081	1082
ω_{11} [cm^{-1}]	1423	1293	1223	1445	1319	1241	1448	1321	1244
ω_{12} [cm^{-1}]	1475	1447	1434	1492	1468	1454	1496	1473	1460
ω_{13} [cm^{-1}]	1479	1448	1435	1496	1468	1455	1500	1475	1461
ω_{14} [cm^{-1}]	2351	2349	2345	2310	2293	2298	2311	2296	2301
ω_{15} [cm^{-1}]	2362	2361	2357	2313	2295	2301	2313	2298	2303
ω_{16} [cm^{-1}]	3118	3135	3138	3075	3104	3116	3078	3110	3119
ω_{17} [cm^{-1}]	3242	3271	3284	3174	3218	3244	3178	3227	3250
ω_{18} [cm^{-1}]	3248	3274	3287	3181	3220	3248	3186	3230	3253

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

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

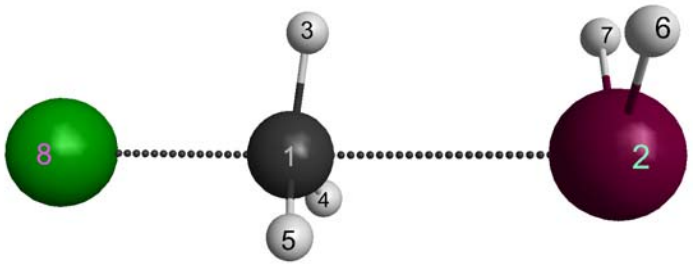


1	C						
2	Y	1	r_1				
3	H	1	r_2	2	a_1		
4	H	1	r_3	2	a_2	3	d_1
5	H	1	r_3	2	a_2	3	$-d_1$
6	P	2	r_4	1	a_3	3	0.0
7	H	6	r_5	2	a_4	3	d_2
8	H	6	r_5	2	a_4	3	$-d_2$

Level[a]	MP2/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVTZ		
System	**$CH_3Cl\cdots PH_2^-$**	**$CH_3Br\cdots PH_2^-$**	**$CH_3I\cdots PH_2^-$**	**$CH_3Cl\cdots PH_2^-$**	**$CH_3Br\cdots PH_2^-$**	**$CH_3I\cdots PH_2^-$**	**$CH_3Cl\cdots PH_2^-$**	**$CH_3Br\cdots PH_2^-$**	**$CH_3I\cdots PH_2^-$**
Energy [E_h]	−841.449736	−797.423272	−676.583118	−841.661840	−797.629932	−676.784349	−841.712608	−797.683865	−676.829452
r_1 [Å]	1.797	2.047	2.325	1.770	2.023	2.296	1.782	2.022	2.296
r_2 [Å]	1.098	1.100	1.102	1.090	1.090	1.091	1.088	1.088	1.090
r_3 [Å]	1.098	1.100	1.102	1.090	1.090	1.091	1.088	1.088	1.090
r_4 [Å]	3.658	3.058	3.017	3.768	3.101	3.016	3.666	3.099	3.007
r_5 [Å]	1.442	1.439	1.436	1.434	1.431	1.429	1.431	1.429	1.426
a_1 [deg]	109.0	108.5	108.4	109.4	108.5	108.5	109.1	108.4	108.4
a_2 [deg]	109.1	108.5	108.4	109.5	108.5	108.5	109.2	108.3	108.3
a_3 [deg]	171.5	179.7	179.7	171.1	180.3	179.9	173.8	180.1	179.9
a_4 [deg]	118.9	94.1	93.5	117.2	92.6	93.6	112.2	92.9	93.7
d_1 [deg]	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0
d_2 [deg]	124.6	133.7	133.7	126.0	133.9	133.8	129.0	133.9	133.8
ZPE [cm^{-1}]	11307	11154	11073	11250	11098	11017	11242	11114	11012
ω_1 [cm^{-1}]	8	10*i*	11*i*	35*i*	18*i*	30	53*i*	39*i*	54*i*
ω_2 [cm^{-1}]	16	84	101	23*i*	90	97	38	89	103
ω_3 [cm^{-1}]	50	92	104	37	93	104	46	89	107
ω_4 [cm^{-1}]	53	99	144	52	103	138	57	96	139
ω_5 [cm^{-1}]	98	283	358	84	253	364	91	257	368
ω_6 [cm^{-1}]	105	288	390	118	261	374	97	263	373
ω_7 [cm^{-1}]	738	441	395	750	460	377	736	465	374
ω_8 [cm^{-1}]	1014	843	717	1048	861	727	1019	862	725
ω_9 [cm^{-1}]	1014	844	719	1048	862	729	1020	863	728
ω_{10} [cm^{-1}]	1083	1085	1095	1089	1085	1094	1081	1087	1092
ω_{11} [cm^{-1}]	1350	1206	1111	1378	1235	1137	1373	1237	1134
ω_{12} [cm^{-1}]	1471	1448	1435	1490	1467	1456	1495	1474	1459
ω_{13} [cm^{-1}]	1472	1448	1435	1490	1469	1456	1495	1475	1460
ω_{14} [cm^{-1}]	2339	2359	2377	2296	2312	2332	2296	2314	2333
ω_{15} [cm^{-1}]	2350	2372	2391	2298	2317	2337	2299	2317	2338
ω_{16} [cm^{-1}]	3079	3057	3042	3049	3040	3023	3053	3044	3025
ω_{17} [cm^{-1}]	3187	3177	3166	3137	3143	3130	3143	3148	3133
ω_{18} [cm^{-1}]	3188	3178	3166	3137	3143	3130	3144	3149	3133

[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 WaldenTS [X = F, Cl, Br] transition states (C_s symmetry) obtained at different levels of theory

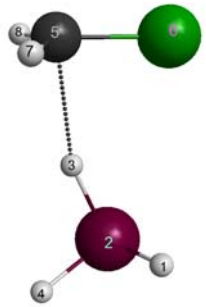


1	C							
2	P	1	r_1					
3	H	1	r_2	2	a_1			
4	H	1	r_3	2	a_2	3	d_1	
5	H	1	r_3	2	a_2	3	$-d_1$	
6	H	2	r_4	1	a_3	3	d_2	
7	H	2	r_4	1	a_3	3	$-d_2$	
8	X	1	r_5	3	a_4	2	180.0	

Level[a]	MP2/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVTZ		
System	$[F{\cdot}CH_3{\cdot}PH_2]^-$	$[Cl{\cdot}CH_3{\cdot}PH_2]^-$	$[Br{\cdot}CH_3{\cdot}PH_2]^-$	$[F{\cdot}CH_3{\cdot}PH_2]^-$	$[Cl{\cdot}CH_3{\cdot}PH_2]^-$	$[Br{\cdot}CH_3{\cdot}PH_2]^-$	$[F{\cdot}CH_3{\cdot}PH_2]^-$	$[Cl{\cdot}CH_3{\cdot}PH_2]^-$	$[Br{\cdot}CH_3{\cdot}PH_2]^-$
Energy [E_h]	−481.433490	−841.460922	−797.430295	−481.668641	−841.669397	−797.636823	−481.710539	−841.721051	−797.690671
r_1 [Å]	2.517	2.779	2.873	2.508	2.769	2.879	2.507	2.768	2.881
r_2 [Å]	1.083	1.085	1.087	1.073	1.075	1.077	1.072	1.074	1.076
r_3 [Å]	1.084	1.086	1.088	1.074	1.075	1.077	1.073	1.074	1.076
r_4 [Å]	1.437	1.438	1.439	1.430	1.431	1.431	1.427	1.428	1.428
r_5 [Å]	1.811	2.111	2.200	1.817	2.126	2.205	1.817	2.123	2.203
a_1 [deg]	87.5	80.5	78.0	87.6	80.6	77.7	87.8	80.8	78.2
a_2 [deg]	86.9	81.3	79.4	87.6	82.0	79.9	87.5	81.9	79.8
a_3 [deg]	95.2	92.0	90.7	94.9	90.9	89.1	95.4	91.6	90.2
a_4 [deg]	92.9	99.0	101.1	92.4	98.5	100.8	92.4	98.5	100.8
d_1 [deg]	120.2	120.2	120.3	120.2	120.2	120.3	120.2	120.2	120.3
d_2 [deg]	46.5	46.2	46.2	46.3	46.0	46.0	46.4	46.1	46.0
ZPE [cm^{-1}]	11677	11348	11195	11544	11233	11122	11538	11232	11090
ω_1 [cm^{-1}]	583i	432i	318i	604i	450i	327i	602i	445i	319i
ω_2 [cm^{-1}]	106	55	42	92	45	78	91	35	12i
ω_3 [cm^{-1}]	201	147	128	198	151	128	192	141	125
ω_4 [cm^{-1}]	217	154	132	211	152	130	211	155	132
ω_5 [cm^{-1}]	270	206	176	257	197	166	257	197	166
ω_6 [cm^{-1}]	435	332	298	431	337	302	428	330	294
ω_7 [cm^{-1}]	452	342	304	445	347	307	440	339	299
ω_8 [cm^{-1}]	1005	921	882	989	897	867	988	902	869
ω_9 [cm^{-1}]	1027	935	893	1010	909	873	1009	913	877
ω_{10} [cm^{-1}]	1063	1021	1015	1048	1001	1015	1046	1011	1023
ω_{11} [cm^{-1}]	1094	1089	1088	1094	1092	1091	1094	1091	1090
ω_{12} [cm^{-1}]	1391	1404	1406	1396	1411	1420	1395	1416	1424
ω_{13} [cm^{-1}]	1392	1404	1407	1396	1411	1421	1395	1416	1424
ω_{14} [cm^{-1}]	2367	2362	2360	2325	2320	2317	2329	2323	2319
ω_{15} [cm^{-1}]	2380	2376	2374	2330	2325	2322	2332	2326	2323
ω_{16} [cm^{-1}]	3178	3184	3169	3161	3168	3154	3162	3169	3156
ω_{17} [cm^{-1}]	3381	3378	3355	3347	3349	3327	3348	3348	3329
ω_{18} [cm^{-1}]	3395	3385	3361	3358	3353	3329	3359	3352	3331

[a] For Br 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

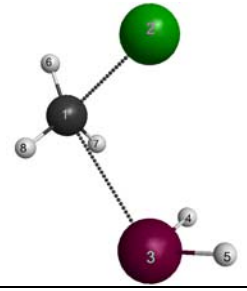


1	H							
2	P	1	r_1					
3	H	2	r_2	1	a_1			
4	H	2	r_3	3	a_2	1	d_1	
5	C	3	r_4	2	a_3	1	d_2	
6	Y	5	r_5	3	a_4	2	d_3	
7	H	5	r_6	6	a_5	2	d_4	
8	H	5	r_7	6	a_6	2	d_5	

Level[a]	MP2/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVTZ			
System	$[FCH_2\cdots HPH_2]^-$	$[ClCH_2\cdots HPH_2]^-$	$[BrCH_2\cdots HPH_2]^-$	$[ICH_2\cdots HPH_2]^-$	$[FCH_2\cdots HPH_2]^-$	$[ClCH_2\cdots HPH_2]^-$	$[BrCH_2\cdots HPH_2]^-$	$[ICH_2\cdots HPH_2]^-$	$[FCH_2\cdots HPH_2]^-$	$[ClCH_2\cdots HPH_2]^-$	$[BrCH_2\cdots HPH_2]^-$	$[ICH_2\cdots HPH_2]^-$
Energy [E_h]	−481.365990	−841.394250	−797.362227	−676.513294	−481.607139	−841.607162	−797.570582	−676.717766	−481.647860	−841.657489	−797.623642	−676.762107
r_1 [Å]	1.431	1.430	1.430	1.430	1.422	1.421	1.421	1.420	1.419	1.418	1.418	1.417
r_2 [Å]	1.572	1.523	1.516	1.496	1.526	1.476	1.472	1.461	1.530	1.477	1.470	1.458
r_3 [Å]	1.434	1.434	1.433	1.433	1.425	1.425	1.425	1.424	1.422	1.423	1.422	1.421
r_4 [Å]	1.793	1.929	1.964	2.062	1.897	2.094	2.132	2.222	1.878	2.076	2.127	2.224
r_5 [Å]	1.438	1.788	1.925	2.106	1.414	1.762	1.918	2.089	1.415	1.768	1.920	2.090
r_6 [Å]	1.088	1.087	1.087	1.088	1.077	1.077	1.076	1.077	1.076	1.075	1.075	1.075
r_7 [Å]	1.088	1.087	1.087	1.088	1.078	1.077	1.077	1.077	1.076	1.075	1.075	1.076
a_1 [deg]	94.0	95.3	95.3	95.4	94.7	95.5	95.5	95.4	94.6	95.6	95.6	95.4
a_2 [deg]	93.0	93.5	93.4	93.7	93.8	94.1	94.1	94.1	93.7	94.2	94.2	94.2
a_3 [deg]	198.6	192.5	189.0	184.6	203.6	199.7	193.7	188.8	202.3	197.6	193.7	189.3
a_4 [deg]	84.7	85.6	86.5	87.9	82.5	82.4	83.9	85.7	83.0	82.8	83.6	85.3
a_5 [deg]	114.0	115.4	115.5	116.1	115.0	116.3	115.8	116.3	114.9	116.1	115.7	116.3
a_6 [deg]	113.9	115.4	115.5	116.1	114.9	116.3	115.8	116.3	114.8	116.1	115.6	116.2
d_1 [deg]	93.3	93.5	93.6	93.7	93.3	93.5	93.5	93.6	93.5	93.7	93.7	93.7
d_2 [deg]	244.8	249.6	250.6	255.7	244.0	247.9	247.7	249.1	243.4	246.9	247.0	246.6
d_3 [deg]	2.4	−1.6	−3.1	−9.9	1.9	−0.9	−2.0	−4.8	2.2	−0.7	−1.5	−3.1
d_4 [deg]	77.7	80.7	81.6	83.1	82.9	84.2	85.0	85.3	82.5	84.5	85.2	85.5
d_5 [deg]	282.0	279.3	278.3	276.7	276.4	274.5	273.6	273.2	276.9	274.5	273.7	273.2
ZPE [cm^{-1}]	10497	10381	10276	10219	10436	10361	10279	10194	10423	10337	10260	10160
ω_1 [cm^{-1}]	1013*i*	841*i*	837*i*	810*i*	965*i*	807*i*	847*i*	824*i*	978*i*	827*i*	860*i*	834*i*
ω_2 [cm^{-1}]	83	78	65	57	77	70	55	43	75	69	56	53
ω_3 [cm^{-1}]	97	108	101	91	112	111	138	114	102	112	124	86
ω_4 [cm^{-1}]	253	181	161	134	166	142	141	128	177	143	137	121
ω_5 [cm^{-1}]	284	252	245	223	243	197	204	187	244	205	202	171
ω_6 [cm^{-1}]	449	416	400	363	417	354	347	315	420	357	345	307
ω_7 [cm^{-1}]	491	466	446	409	470	434	404	362	472	425	401	357
ω_8 [cm^{-1}]	936	738	644	593	958	730	620	575	953	722	616	572
ω_9 [cm^{-1}]	1025	964	912	855	1035	969	907	849	1038	961	902	840
ω_{10} [cm^{-1}]	1092	1041	1038	1031	1093	1028	1031	1026	1095	1032	1033	1026
ω_{11} [cm^{-1}]	1120	1133	1135	1138	1124	1120	1128	1128	1126	1123	1127	1127
ω_{12} [cm^{-1}]	1162	1188	1177	1167	1178	1171	1164	1156	1181	1167	1164	1156
ω_{13} [cm^{-1}]	1212	1362	1339	1317	1333	1370	1325	1304	1288	1354	1317	1294
ω_{14} [cm^{-1}]	1406	1434	1482	1656	1412	1771	1809	1924	1411	1734	1800	1924
ω_{15} [cm^{-1}]	2396	2399	2402	2409	2363	2360	2368	2373	2366	2365	2370	2375
ω_{16} [cm^{-1}]	2419	2426	2427	2432	2383	2393	2396	2400	2386	2397	2400	2404
ω_{17} [cm^{-1}]	3201	3208	3206	3199	3172	3173	3179	3172	3175	3177	3181	3172
ω_{18} [cm^{-1}]	3368	3369	3372	3365	3335	3326	3343	3332	3336	3331	3345	3333

[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_1 symmetry) obtained at different levels of theory

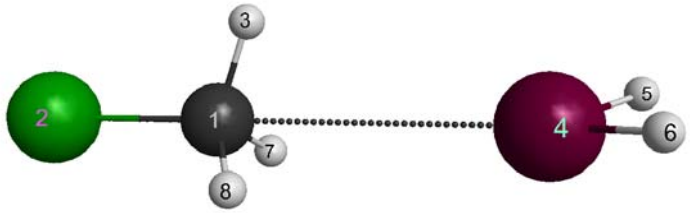


1	C							
2	Y	1	r_1					
3	P	1	r_2	2	a_1			
4	H	3	r_3	1	a_2	2	d_1	
5	H	3	r_4	1	a_3	2	d_2	
6	H	1	r_5	2	a_4	3	d_3	
7	H	1	r_6	3	a_5	2	d_4	
8	H	1	r_7	3	a_6	2	$-d_5$	

Level[a]	MP2/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVDZ		CCSD(T)-F12b/aug-cc-pVTZ	
System	**$[H_2P\cdots CH_3\cdots F]^-$**	**$[H_2P\cdots CH_3\cdots Cl]^-$**	**$[H_2P\cdots CH_3\cdots Br]^-$**	**$[H_2P\cdots CH_3\cdots I]^-$**	**$[H_2P\cdots CH_3\cdots F]^-$**	**$[H_2P\cdots CH_3\cdots Cl]^-$**	**$[H_2P\cdots CH_3\cdots F]^-$**	**$[H_2P\cdots CH_3\cdots Cl]^-$**
Energy [E_h]	−481.376644	−841.399466	−797.371471	−676.522811	−481.612142	−841.613083	−481.654470	−841.663448
r_1 [Å]	1.770	2.276	2.418	2.629	1.802	2.370	1.820	2.377
r_2 [Å]	2.483	2.685	2.717	2.758	2.519	2.939	2.542	2.884
r_3 [Å]	1.435	1.434	1.433	1.432	1.428	1.424	1.437	1.422
r_4 [Å]	1.436	1.437	1.438	1.440	1.426	1.427	1.421	1.425
r_5 [Å]	1.106	1.096	1.096	1.096	1.092	1.080	1.090	1.079
r_6[Å]	1.109	1.096	1.096	1.096	1.096	1.083	1.086	1.081
r_7 [Å]	1.096	1.093	1.094	1.094	1.084	1.081	1.083	1.080
a_1 [deg]	80.4	87.7	89.3	92.3	79.1	85.1	74.4	86.5
a_2 [deg]	88.2	84.5	83.5	82.0	88.2	77.3	90.0	79.0
a_3 [deg]	117.7	123.7	125.3	128.7	115.1	122.9	92.2	124.4
a_4 [deg]	82.9	79.4	79.4	79.1	81.5	80.8	79.1	78.8
a_5 [deg]	73.5	69.8	69.3	67.8	73.4	66.7	79.2	66.8
a_6 [deg]	93.0	79.5	78.4	77.1	92.1	71.9	86.4	72.8
d_1 [deg]	256.8	265.5	267.1	269.8	252.7	273.1	199.8	271.7
d_2 [deg]	−11.2	−5.4	−4.9	−4.0	−15.6	−2.8	−68.3	−3.3
d_3 [deg]	201.5	188.0	187.0	186.6	201.6	183.5	189.3	184.2
d_4 [deg]	148.1	127.6	125.7	123.8	147.8	116.8	133.9	117.9
d_5 [deg]	102.4	112.2	113.1	113.3	101.3	113.5	113.3	113.2
ZPE [cm^{-1}]	11462	11233	11168	11099	11296	10832	11274	11027
ω_1 [cm^{-1}]	647*i*	657*i*	602*i*	585*i*	664*i*	642*i*	671*i*	574*i*
ω_2 [cm^{-1}]	108	100	101	87	65	77	112	128*i*
ω_3 [cm^{-1}]	206	135	110	111	198	115	153	127
ω_4 [cm^{-1}]	248	193	195	192	230	138	205	219
ω_5 [cm^{-1}]	307	238	231	225	263	205	317	286
ω_6 [cm^{-1}]	466	384	371	351	440	242	389	311
ω_7 [cm^{-1}]	512	415	399	383	463	337	491	372
ω_8 [cm^{-1}]	851	724	701	673	827	570	780	614
ω_9 [cm^{-1}]	995	834	800	767	957	703	913	733
ω_{10} [cm^{-1}]	1111	1108	1099	1076	1110	946	1102	990
ω_{11} [cm^{-1}]	1227	1123	1109	1112	1195	1116	1200	1131
ω_{12} [cm^{-1}]	1419	1421	1421	1420	1430	1425	1451	1438
ω_{13} [cm^{-1}]	1508	1481	1478	1475	1505	1445	1489	1463
ω_{14} [cm^{-1}]	2379	2380	2377	2369	2334	2355	2260	2360
ω_{15} [cm^{-1}]	2394	2404	2408	2413	2350	2368	2369	2370
ω_{16} [cm^{-1}]	2973	3085	3088	3092	2991	3108	3019	3117
ω_{17} [cm^{-1}]	3023	3186	3193	3201	3044	3248	3106	3253
ω_{18} [cm^{-1}]	3197	3254	3253	3251	3191	3265	3191	3270

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

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

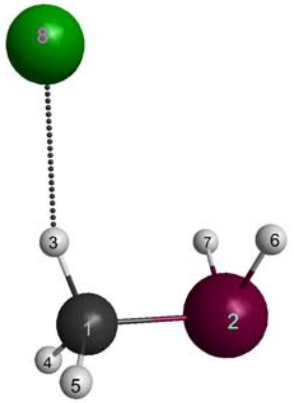


1	C						
2	Y	1	r_1				
3	H	1	r_2	2	a_1		
4	P	1	r_3	3	a_2	2	180.0
5	H	4	r_4	1	a_3	3	d_1
6	H	4	r_4	1	a_3	3	$-d_1$
7	H	1	r_5	2	a_4	3	d_2
8	H	1	r_5	2	a_4	3	$-d_2$

Level[a]	MP2/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVTZ		
System	$[ClCH_3\cdots PH_2]^-$	$[BrCH_3\cdots PH_2]^-$	$[ICH_3\cdots PH_2]^-$	$[ClCH_3\cdots PH_2]^-$	$[BrCH_3\cdots PH_2]^-$	$[ICH_3\cdots PH_2]^-$	$[ClCH_3\cdots PH_2]^-$	$[BrCH_3\cdots PH_2]^-$	$[ICH_3\cdots PH_2]^-$
Energy [E_h]	−841.467047	−797.431309	−676.576165	−841.677382	−797.637952	−676.777981	−841.728612	−797.691626	−676.822593
r_1 [Å]	1.827	1.980	2.187	1.803	1.969	2.170	1.810	1.972	2.172
r_2 [Å]	1.093	1.093	1.093	1.084	1.083	1.083	1.082	1.081	1.082
r_3 [Å]	3.362	3.333	3.306	3.394	3.349	3.328	3.394	3.350	3.329
r_4 [Å]	1.439	1.439	1.439	1.431	1.431	1.430	1.429	1.428	1.428
r_5 [Å]	1.094	1.093	1.094	1.085	1.084	1.084	1.083	1.082	1.082
a_1 [deg]	108.6	108.2	108.1	109.1	108.3	108.1	108.7	107.9	107.8
a_2 [deg]	69.1	68.6	67.4	67.9	68.9	67.5	71.6	70.3	69.0
a_3 [deg]	133.2	133.3	133.3	132.6	133.4	133.5	132.8	133.4	133.5
a_4 [deg]	108.0	107.6	107.4	108.6	107.7	107.5	108.4	107.5	107.3
d_1 [deg]	−84.2	−85.6	−86.2	−79.5	−85.4	−86.3	−80.5	−85.4	−86.6
d_2 [deg]	−120.3	−120.3	−120.3	−120.2	−120.3	−120.3	−120.2	−120.3	−120.3
ZPE [cm^{-1}]	11344	11198	11066	11258	11167	11022*i*	11267	11123	11004
ω_1 [cm^{-1}]	87*i*	120*i*	152*i*	56*i*	112*i*	143*i*	55*i*	98*i*	133*i*
ω_2 [cm^{-1}]	14*i*	7	19	43*i*	45	38	49*i*	36*i*	23
ω_3 [cm^{-1}]	52	53	55	47	66	55	23	31	47
ω_4 [cm^{-1}]	73	65	55	47	71	66	70	62	56
ω_5 [cm^{-1}]	96	90	88	86	89	86	86	81	80
ω_6 [cm^{-1}]	98	92	89	96	93	90	94	87	84
ω_7 [cm^{-1}]	673	564	496	677	563	493	676	558	489
ω_8 [cm^{-1}]	998	938	873	1009	938	872	1003	939	872
ω_9 [cm^{-1}]	1007	947	884	1021	948	882	1010	946	881
ω_{10} [cm^{-1}]	1081	1079	1077	1083	1084	1082	1082	1081	1080
ω_{11} [cm^{-1}]	1323	1279	1232	1345	1296	1247	1349	1297	1247
ω_{12} [cm^{-1}]	1450	1442	1433	1469	1461	1454	1477	1467	1458
ω_{13} [cm^{-1}]	1455	1447	1439	1476	1468	1460	1482	1473	1464
ω_{14} [cm^{-1}]	2355	2355	2356	2314	2316	2316	2314	2316	2316
ω_{15} [cm^{-1}]	2367	2368	2369	2318	2321	2321	2318	2320	2321
ω_{16} [cm^{-1}]	3131	3132	3130	3101	3112	3111	3108	3114	3113
ω_{17} [cm^{-1}]	3259	3265	3266	3208	3228	3231	3218	3234	3235
ω_{18} [cm^{-1}]	3268	3274	3273	3218	3236	3238	3225	3240	3241

[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 S7. Energies, structures, and frequencies for the PostHMIN2 [Y = F, Cl, Br, I] H-bonded complexes (C_s symmetry) obtained at different levels of theory

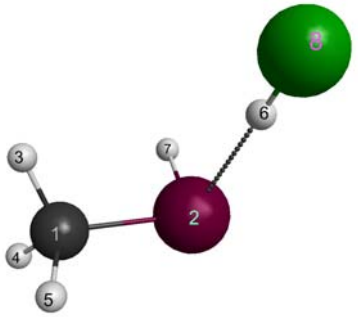


1	C						
2	P	1	r_1				
3	H	1	r_2	2	a_1		
4	H	1	r_3	2	a_2	3	d_1
5	H	1	r_3	2	a_2	3	$-d_1$
6	H	2	r_4	1	a_3	3	d_2
7	H	2	r_4	1	a_3	3	$-d_2$
8	Y	3	r_5	1	a_4	2	0.0

Level[a]	MP2/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVTZ			
System	**F^-···HCH_2PH_2**	**Cl^-···HCH_2PH_2**	**Br^-···HCH_2PH_2**	**I^-···HCH_2PH_2**	**F^-···HCH_2PH_2**	**Cl^-···HCH_2PH_2**	**Br^-···HCH_2PH_2**	**I^-···HCH_2PH_2**	**F^-···HCH_2PH_2**	**Cl^-···HCH_2PH_2**	**Br^-···HCH_2PH_2**	**I^-···HCH_2PH_2**
Energy [E_h]	−481.489464	−841.537586	−797.510112	−676.663440	−481.725542	−841.745738	−797.717443	−676.866257	−481.766688	−841.796812	−797.770687	−676.910599
r_1 [Å]	1.868	1.871	1.871	1.872	1.846	1.850	1.851	1.851	1.844	1.849	1.849	1.850
r_2 [Å]	1.132	1.105	1.103	1.102	1.124	1.096	1.094	1.093	1.123	1.095	1.093	1.091
r_3 [Å]	1.104	1.102	1.102	1.102	1.096	1.094	1.094	1.093	1.094	1.092	1.092	1.092
r_4 [Å]	1.429	1.427	1.427	1.426	1.420	1.418	1.418	1.418	1.417	1.415	1.415	1.415
r_5 [Å]	1.698	2.451	2.631	2.888	1.682	2.467	2.652	2.909	1.682	2.456	2.663	2.945
a_1 [deg]	111.8	110.7	110.6	110.8	111.6	110.2	110.5	110.9	111.7	110.3	110.5	110.9
a_2 [deg]	107.5	108.5	108.7	108.8	107.8	108.8	108.9	108.9	107.7	108.7	108.8	108.8
a_3 [deg]	97.9	97.3	97.2	97.1	98.3	97.4	97.4	97.4	98.4	97.6	97.5	97.5
a_4 [deg]	176.8	166.3	162.8	160.4	175.9	159.1	158.5	157.9	176.2	160.2	157.1	155.3
d_1 [deg]	122.4	121.5	121.4	121.3	122.3	121.3	121.3	121.2	122.3	121.4	121.3	121.2
d_2 [deg]	47.1	47.0	47.0	47.0	47.0	46.9	46.9	46.9	47.1	47.0	47.0	47.0
ZPE [cm^{-1}]	12029	12105	12078	12060	11950	12004	11994	12000	11969	12008	11982	12008
ω_1 [cm^{-1}]	75	31	27	23*i*	66	29*i*	40*i*	18*i*	73	19*i*	50*i*	41*i*
ω_2 [cm^{-1}]	106	54	27	29	101	36	29	37	99	28	6	33
ω_3 [cm^{-1}]	241	148	125	110	249	139	128	101	249	147	129	105
ω_4 [cm^{-1}]	315	256	247	239	314	247	236	240	309	241	224	231
ω_5 [cm^{-1}]	684	683	683	683	695	693	692	692	695	692	690	692
ω_6 [cm^{-1}]	700	694	694	694	701	698	695	697	702	694	691	694
ω_7 [cm^{-1}]	762	756	755	753	765	758	753	754	764	755	751	752
ω_8 [cm^{-1}]	1007	998	996	993	1014	1004	1002	1002	1017	1005	1000	1001
ω_9 [cm^{-1}]	1049	1040	1039	1038	1051	1045	1041	1043	1052	1043	1040	1042
ω_{10} [cm^{-1}]	1113	1113	1112	1112	1105	1103	1105	1104	1108	1106	1106	1106
ω_{11} [cm^{-1}]	1349	1310	1304	1301	1369	1325	1324	1325	1373	1329	1325	1325
ω_{12} [cm^{-1}]	1455	1450	1449	1449	1465	1461	1463	1464	1469	1466	1466	1469
ω_{13} [cm^{-1}]	1507	1480	1476	1472	1521	1495	1491	1488	1527	1501	1496	1493
ω_{14} [cm^{-1}]	2426	2442	2444	2444	2387	2409	2409	2409	2393	2413	2414	2416
ω_{15} [cm^{-1}]	2437	2453	2455	2455	2392	2414	2413	2414	2397	2417	2417	2419
ω_{16} [cm^{-1}]	2637	3014	3027	3038	2603	2988	3001	3011	2600	2985	3001	3014
ω_{17} [cm^{-1}]	3073	3137	3146	3154	3031	3094	3102	3106	3035	3093	3104	3109
ω_{18} [cm^{-1}]	3123	3149	3151	3156	3072	3099	3103	3113	3077	3102	3105	3115

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

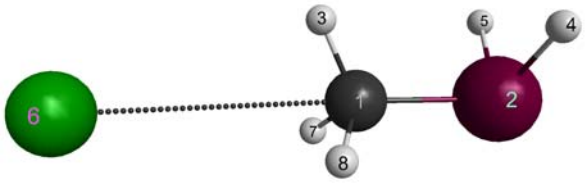
Table S8. Energies, structures, and frequencies for the PostHMIN [Y = F] H-bonded complexes (C_1 symmetry) obtained at different levels of theory



1	C						
2	P	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	MP2/aug-cc-pVDZ	CCSD(T)-F12b/aug-cc-pVDZ	CCSD(T)-F12b/aug-cc-pVTZ
Energy [E_h]	−481.499763	−481.736962	−481.778412
r_1 [Å]	1.910	1.892	1.891
r_2 [Å]	1.104	1.096	1.094
r_3 [Å]	1.105	1.096	1.094
r_4 [Å]	1.105	1.096	1.094
r_5 [Å]	2.010	2.044	2.045
r_6 [Å]	1.440	1.432	1.430
r_7 [Å]	1.018	0.997	0.996
a_1 [deg]	113.0	113.1	113.1
a_2 [deg]	113.0	113.0	112.8
a_3 [deg]	107.6	107.8	107.6
a_4 [deg]	96.4	97.7	98.5
a_5 [deg]	95.7	95.8	95.9
a_6 [deg]	183.1	182.8	182.6
d_1 [deg]	123.6	123.5	123.5
d_2 [deg]	−118.2	−118.3	−118.4
d_3 [deg]	40.2	40.5	40.6
d_4 [deg]	−58.2	−58.7	−58.7
d_5 [deg]	−64.8	−65.1	−59.1
ZPE [cm^{-1}]	11949	12015	12060
ω_1 [cm^{-1}]	66	60	66
ω_2 [cm^{-1}]	124	103	125
ω_3 [cm^{-1}]	232	228	231
ω_4 [cm^{-1}]	337	322	331
ω_5 [cm^{-1}]	648	655	655
ω_6 [cm^{-1}]	701	702	705
ω_7 [cm^{-1}]	855	855	858
ω_8 [cm^{-1}]	975	962	968
ω_9 [cm^{-1}]	1003	995	996
ω_{10} [cm^{-1}]	1016	1007	1010
ω_{11} [cm^{-1}]	1264	1286	1286
ω_{12} [cm^{-1}]	1450	1464	1471
ω_{13} [cm^{-1}]	1464	1478	1485
ω_{14} [cm^{-1}]	2190	2296	2299
ω_{15} [cm^{-1}]	2345	2525	2530
ω_{16} [cm^{-1}]	3019	2987	2989
ω_{17} [cm^{-1}]	3096	3044	3048
ω_{18} [cm^{-1}]	3113	3061	3066

Table S9. Energies, structures, and frequencies for the WaldenPostMIN [Y = Br] ion-dipole complexes (C_s symmetry) obtained at different levels of theory



1	C							
2	P	1	r_1					
3	H	1	r_2	2	a_1			
4	H	2	r_3	1	a_2	3	d_1	
5	H	2	r_3	1	a_2	3	$-d_1$	
6	Y	1	r_4	3	a_3	2	180.0	
7	H	1	r_5	2	a_4	3	d_2	
8	H	1	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
Energy [E_h]	−797.507242	−797.714844	−797.768135
r_1 [Å]	1.870	1.848	1.847
r_2 [Å]	1.096	1.088	1.086
r_3 [Å]	1.430	1.422	1.419
r_4 [Å]	3.565	3.565	3.571
r_5 [Å]	1.099	1.091	1.089
a_1 [deg]	114.4	114.6	114.5
a_2 [deg]	98.7	98.9	99.0
a_3 [deg]	67.3	67.1	67.2
a_4 [deg]	109.7	109.9	109.8
d_1 [deg]	47.3	47.1	47.2
d_2 [deg]	121.6	121.6	121.7
ZPE [cm^{-1}]	11993	11938	11942
ω_1 [cm^{-1}]	20i	25i	28i
ω_2 [cm^{-1}]	9i	22	17i
ω_3 [cm^{-1}]	67	65	64
ω_4 [cm^{-1}]	232	230	232
ω_5 [cm^{-1}]	669	670	670
ω_6 [cm^{-1}]	673	683	682
ω_7 [cm^{-1}]	722	726	726
ω_8 [cm^{-1}]	965	974	974
ω_9 [cm^{-1}]	1014	1019	1019
ω_{10} [cm^{-1}]	1123	1115	1119
ω_{11} [cm^{-1}]	1292	1315	1316
ω_{12} [cm^{-1}]	1442	14601	1464
ω_{13} [cm^{-1}]	1445	1461	1469
ω_{14} [cm^{-1}]	2416	2379	2385
ω_{15} [cm^{-1}]	2427	2384	2388
ω_{16} [cm^{-1}]	3098	3067	3067
ω_{17} [cm^{-1}]	3190	3142	3143
ω_{18} [cm^{-1}]	3212	3165	3166

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