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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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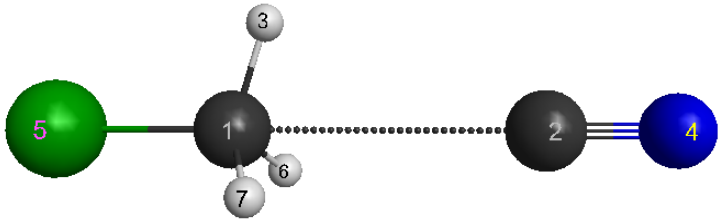
Content

Table S1. Energies, structures, and frequencies for the PreMIN [Y = F, Cl, Br, I] ion-dipole complexes (C_{3v} symmetry)[a] obtained at different levels of theory



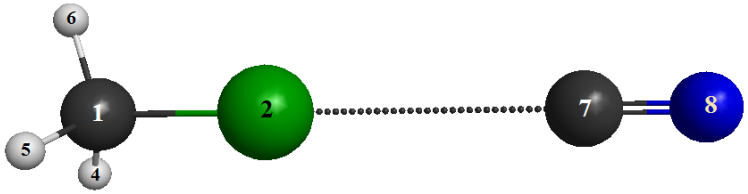
1	C							
2	C	1	r_1					
3	H	1	r_2	2	a_1			
4	N	2	r_3	1	a_2	3	0.0	
5	Y	1	r_4	3	a_3	2	180.0	
6	H	1	r_5	2	a_4	3	d_1	
7	H	1	r_5	2	a_4	3	$-d_1$	

Level[b]	**MP2/aug-cc-pVDZ**				**CCSD(T)-F12b/aug-cc-pVDZ**				**CCSD(T)-F12b/aug-cc-pVTZ**			
System	**$FCH_3\cdots CN^-$**	**$ClCH_3\cdots CN^-$**	**$BrCH_3\cdots CN^-$**	**$ICH_3\cdots CN^-$**	**$FCH_3\cdots CN^-$**	**$ClCH_3\cdots CN^-$**	**$BrCH_3\cdots CN^-$**	**$ICH_3\cdots CN^-$**	**$FCH_3\cdots CN^-$**	**$ClCH_3\cdots CN^-$**	**$BrCH_3\cdots CN^-$**	**$ICH_3\cdots CN^-$**
Energy [E_h]	−232.053046	−592.062498	−548.026702	−427.171385	−232.327093	−592.306812	−548.267482	−427.407379	−232.363589	−592.353217	−548.316259	−427.447080
r_1 [Å]	3.087	3.052	3.021	2.995	3.096	3.073	3.023	3.004	3.087	3.061	3.014	2.994
r_2 [Å]	1.094	1.092	1.092	1.092	1.087	1.084	1.082	1.082	1.085	1.082	1.081	1.081
r_3 [Å]	1.207	1.206	1.206	1.206	1.179	1.179	1.179	1.179	1.179	1.179	1.179	1.179
r_4 [Å]	1.440	1.835	1.989	2.198	1.410	1.810	1.979	2.181	1.411	1.816	1.981	2.184
r_5 [Å]	1.094	1.092	1.092	1.092	1.087	1.084	1.082	1.082	1.085	1.082	1.081	1.081
a_1 [deg]	71.6	71.8	72.3	72.6	70.9	71.3	72.3	72.5	71.0	71.5	72.4	72.7
a_2 [deg]	179.4	179.8	180.0	180.0	180.1	181.1	180.1	180.1	179.6	180.2	180.0	180.0
a_3 [deg]	108.4	108.1	107.7	107.4	109.1	108.7	107.7	107.5	109.0	108.5	107.6	107.3
a_4 [deg]	71.6	71.9	72.3	72.6	70.9	71.3	72.3	72.5	71.0	71.5	72.4	72.7
d_1 [deg]	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0
ZPE [cm^{-1}]	9803	9431	9281	9136	9838	9469	9357	9189	9846	9470	9329	9178
ω_1 [cm^{-1}]	28	23	23	18	31	35	39	31	31	23	26	20
ω_2 [cm^{-1}]	28	23	23	18	31	36	42	31	32	25	26	21
ω_3 [cm^{-1}]	115	101	95	87	113	87	95	85	112	90	91	83
ω_4 [cm^{-1}]	129	101	95	87	118	88	106	85	122	93	92	84
ω_5 [cm^{-1}]	129	111	103	100	119	109	108	99	123	108	102	97
ω_6 [cm^{-1}]	937	652	542	472	987	658	538	468	980	657	534	463
ω_7 [cm^{-1}]	1146	999	939	876	1163	1007	942	873	1162	999	936	870
ω_8 [cm^{-1}]	1146	999	939	876	1163	1007	943	873	1162	999	937	870
ω_9 [cm^{-1}]	1409	1304	1258	1208	1429	1326	1271	1221	1431	1329	1273	1221
ω_{10} [cm^{-1}]	1474	1448	1439	1430	1489	1469	1462	1452	1494	1475	1465	1456
ω_{11} [cm^{-1}]	1474	1448	1439	1431	1490	1469	1463	1452	1494	1476	1466	1456
ω_{12} [cm^{-1}]	1952	1952	1952	1952	2079	2080	2082	2082	2076	2077	2078	2078
ω_{13} [cm^{-1}]	3128	3144	3145	3144	3084	3114	3124	3124	3087	3119	3126	3126
ω_{14} [cm^{-1}]	3257	3279	3285	3287	3189	3227	3249	3251	3193	3235	3252	3255
ω_{15} [cm^{-1}]	3257	3279	3285	3287	3189	3228	3249	3251	3193	3235	3252	3255

[a] The computations are performed using C_s symmetry, but the C_{3v} symmetry, with collinear Y(5), C(1), C(2), N(4) atoms, is numerically obtained.

[b] For Br and I 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_{3v} symmetry) obtained at different levels of theory

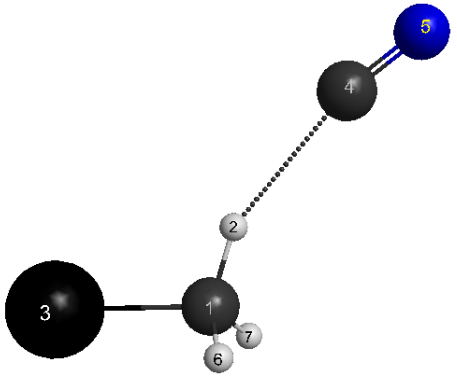


1	C						
2	Y	1	r_1				
3	Q	2	1.0	1	90.0		
4	H	1	r_2	2	a_1	3	0.0
5	H	1	r_2	2	a_1	4	120.0
6	H	1	r_2	2	a_1	4	−120.0
7	C	2	r_3	3	90.0	1	180.0
8	N	2	r_4	3	90.0	1	180.0

Level[a]	**MP2/aug-cc-pVDZ**			**CCSD(T)-F12b/aug-cc-pVDZ**			**CCSD(T)-F12b/aug-cc-pVTZ**		
System	**$CH_3Cl\cdots CN^-$**	**$CH_3Br\cdots CN^-$**	**$CH_3I\cdots CN^-$**	**$CH_3Cl\cdots CN^-$**	**$CH_3Br\cdots CN^-$**	**$CH_3I\cdots CN^-$**	**$CH_3Cl\cdots CN^-$**	**$CH_3Br\cdots CN^-$**	**$CH_3I\cdots CN^-$**
Energy [E_h]	−592.044409	−548.015486	−427.171138	−592.290589	−548.256788	−427.407263	−592.336456	−548.305647	−427.447121
r_1 [Å]	1.792	1.966	2.216	1.770	1.958	2.200	1.778	1.960	2.200
r_2 [Å]	1.099	1.099	1.100	1.090	1.089	1.090	1.088	1.087	1.088
r_3 [Å]	3.274	2.949	2.784	3.179	2.924	2.774	3.218	2.913	2.772
r_4 [Å]	4.481	4.155	3.988	4.359	4.102	3.950	4.398	4.091	3.948
a_1 [deg]	109.2	109.2	109.3	109.6	109.1	109.2	109.3	108.9	109.0
ZPE [cm^{-1}]	9386	9272	9129	9418	9338	9185	9454	9333	9181
ω_1 [cm^{-1}]	24	50	68	35	52	72	35	55	68
ω_2 [cm^{-1}]	24	50	68	37	66	72	36	55	68
ω_3 [cm^{-1}]	68	100	130	59	104	134	69	104	135
ω_4 [cm^{-1}]	90	137	182	60	145	189	97	143	183
ω_5 [cm^{-1}]	90	137	182	80	148	189	97	143	183
ω_6 [cm^{-1}]	753	600	488	754	594	489	751	593	488
ω_7 [cm^{-1}]	1018	929	819	1037	934	820	1025	931	819
ω_8 [cm^{-1}]	1018	929	819	1037	936	820	1025	931	819
ω_9 [cm^{-1}]	1354	1292	1216	1375	1304	1228	1378	1304	1225
ω_{10} [cm^{-1}]	1472	1462	1452	1490	1482	1470	1497	1486	1475
ω_{11} [cm^{-1}]	1472	1462	1452	1491	1484	1471	1497	1486	1475
ω_{12} [cm^{-1}]	1947	1955	1969	2073	2084	2102	2069	2081	2098
ω_{13} [cm^{-1}]	3077	3074	3064	3045	3052	3041	3052	3054	3043
ω_{14} [cm^{-1}]	3183	3184	3175	3131	3146	3138	3140	3150	3141
ω_{15} [cm^{-1}]	3183	3184	3175	3131	3146	3138	3140	3150	3141

[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 HMIN1 [Y = Br, I] H-bonded complexes (C_s symmetry) obtained at different levels of theory

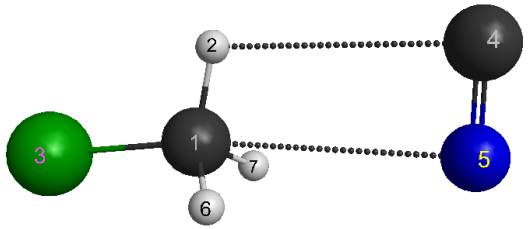


1	C						
2	H	1	r_1				
3	Y	1	r_2	2	a_1		
4	C	2	r_3	1	a_2	3	180.0
5	N	4	r_4	2	a_3	1	0.0
6	H	1	r_5	3	a_4	2	d_1
7	H	1	r_5	3	a_4	2	$-d_1$

Level[a]	**MP2/aug-cc-pVDZ**		**CCSD(T)-F12b/aug-cc-pVDZ**		**CCSD(T)-F12b/aug-cc-pVTZ**	
System	**$BrCH_3\cdots CN^-$**	**$ICH_3\cdots CN^-$**	**$BrCH_3\cdots CN^-$**	**$ICH_3\cdots CN^-$**	**$BrCH_3\cdots CN^-$**	**$ICH_3\cdots CN^-$**
Energy [E_h]	−548.025289	−427.170680	−548.266155	−427.406722	−548.314890	−427.446322
r_1 [Å]	1.101	1.106	1.089	1.095	1.088	1.093
r_2 [Å]	1.968	2.171	1.960	2.155	1.962	2.157
r_3 [Å]	2.331	2.253	2.395	2.277	2.388	2.286
r_4 [Å]	1.206	1.206	1.179	1.179	1.179	1.179
r_5 [Å]	1.096	1.097	1.086	1.087	1.084	1.085
a_1 [deg]	110.0	109.1	110.3	109.3	110.0	109.2
a_2 [deg]	151.5	162.0	141.4	159.5	140.7	156.6
a_3 [deg]	163.2	167.6	169.3	171.7	163.9	167.8
a_4 [deg]	106.6	106.3	106.7	106.3	106.6	106.2
d_1 [deg]	120.7	120.8	120.5	120.7	120.5	120.7
ZPE [cm^{-1}]	9322	9231	9340	9276	9340	9255
ω_1 [cm^{-1}]	16	28	8*i*	35	11*i*	35
ω_2 [cm^{-1}]	37	46	38	56	35	44
ω_3 [cm^{-1}]	44	58	46	69	37	56
ω_4 [cm^{-1}]	143	160	126	153	129	152
ω_5 [cm^{-1}]	187	217	159	196	148	180
ω_6 [cm^{-1}]	594	531	588	527	584	523
ω_7 [cm^{-1}]	953	919	940	914	942	909
ω_8 [cm^{-1}]	980	921	977	918	976	915
ω_9 [cm^{-1}]	1334	1305	1335	1311	1337	1308
ω_{10} [cm^{-1}]	1453	1447	1468	1463	1473	1466
ω_{11} [cm^{-1}]	1481	1481	1492	1497	1499	1499
ω_{12} [cm^{-1}]	1952	1954	2081	2084	2077	2080
ω_{13} [cm^{-1}]	3052	3001	3059	2994	3061	3000
ω_{14} [cm^{-1}]	3192	3174	3178	3146	3181	3150
ω_{15} [cm^{-1}]	3224	3221	3194	3188	3200	3193

[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 HMIN2 [Y = F, Cl, Br, I] H-bonded complexes (C_s symmetry) obtained at different levels of theory

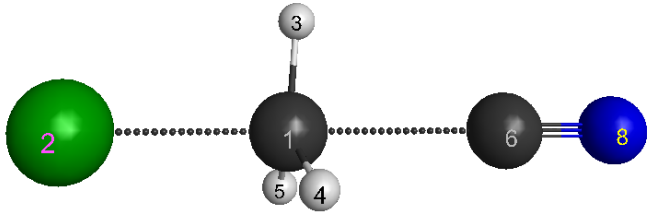


1	C						
2	H	1	r_1				
3	Y	1	r_2	2	a_1		
4	C	2	r_3	1	a_2	3	180.0
5	N	4	r_4	2	a_3	1	0.0
6	H	1	r_5	3	a_4	2	d_1
7	H	1	r_5	3	a_4	2	$-d_1$

Level[a]	**MP2/aug-cc-pVDZ**				**CCSD(T)-F12b/aug-cc-pVDZ**				**CCSD(T)-F12b/aug-cc-pVTZ**			
System	**$FCH_3\cdots CN^-$**	**$ClCH_3\cdots CN^-$**	**$BrCH_3\cdots CN^-$**	**$ICH_3\cdots CN^-$**	**$FCH_3\cdots CN^-$**	**$ClCH_3\cdots CN^-$**	**$BrCH_3\cdots CN^-$**	**$ICH_3\cdots CN^-$**	**$FCH_3\cdots CN^-$**	**$ClCH_3\cdots CN^-$**	**$BrCH_3\cdots CN^-$**	**$ICH_3\cdots CN^-$**
Energy [E_h]	−232.054023	−592.063847	−548.028010	−427.172721	−232.327906	−592.307919	−548.268516	−427.408458	−232.364358	−592.354294	−548.317302	−427.448180
r_1 [Å]	1.095	1.093	1.093	1.093	1.087	1.085	1.083	1.084	1.086	1.083	1.082	1.082
r_2 [Å]	1.439	1.831	1.983	2.189	1.409	1.807	1.972	2.173	1.411	1.813	1.975	2.175
r_3 [Å]	2.887	2.809	2.787	2.765	2.883	2.829	2.807	2.782	2.875	2.823	2.800	2.774
r_4 [Å]	1.208	1.208	1.208	1.208	1.180	1.180	1.180	1.180	1.180	1.180	1.180	1.180
r_5 [Å]	1.095	1.093	1.092	1.093	1.087	1.084	1.083	1.082	1.085	1.082	1.081	1.081
a_1 [deg]	108.6	108.4	108.0	107.9	109.2	108.9	108.0	107.8	109.1	108.6	107.8	107.7
a_2 [deg]	104.7	103.8	102.6	102.4	104.7	103.1	102.2	102.1	104.5	103.3	102.2	102.0
a_3 [deg]	81.6	85.5	87.2	88.0	83.0	86.7	87.1	88.2	83.3	86.3	87.1	88.6
a_4 [deg]	108.4	108.1	107.7	107.5	109.0	108.7	107.8	107.6	109.0	108.5	107.6	107.4
d_1 [deg]	120.1	120.1	120.1	120.1	120.1	120.1	120.1	120.1	120.1	120.1	120.1	120.1
ZPE [cm^{-1}]	9799	9446	9293	9154	9832	9454	9351	9199	9857	9478	9334	9203
ω_1 [cm^{-1}]	12*i*	6	20*i*	31*i*	36*i*	42*i*	29	3	31	35*i*	33*i*	10
ω_2 [cm^{-1}]	52	67	68	64	57	44	71	65	58	66	69	66
ω_3 [cm^{-1}]	108	85	79	71	96	66	74	69	100	74	71	69
ω_4 [cm^{-1}]	110	86	79	74	102	75	84	75	104	78	74	74
ω_5 [cm^{-1}]	133	127	116	113	127	122	114	110	127	120	113	109
ω_6 [cm^{-1}]	946	667	562	497	994	670	559	491	987	671	555	488
ω_7 [cm^{-1}]	1149	1002	942	878	1166	1007	941	874	1166	1001	938	873
ω_8 [cm^{-1}]	1151	1005	944	880	1169	1014	944	879	1169	1005	943	878
ω_9 [cm^{-1}]	1425	1322	1279	1234	1445	1343	1292	1244	1446	1346	1294	1246
ω_{10} [cm^{-1}]	1474	1448	1439	1431	1490	1470	1462	1453	1495	1476	1466	1458
ω_{11} [cm^{-1}]	1479	1455	1446	1437	1495	1474	1465	1458	1499	1480	1470	1462
ω_{12} [cm^{-1}]	1943	1942	1941	1940	2070	2069	2069	2068	2067	2066	2065	2065
ω_{13} [cm^{-1}]	3123	3138	3138	3136	3081	3109	3118	3119	3084	3114	3120	3119
ω_{14} [cm^{-1}]	3252	3271	3276	3276	3186	3220	3238	3242	3190	3228	3243	3244
ω_{15} [cm^{-1}]	3252	3273	3278	3278	3186	3224	3242	3247	3191	3231	3247	3247

[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 WaldenTS [Y = F, Cl, Br, I] transition states (C_{3v} symmetry) obtained at different levels of theory

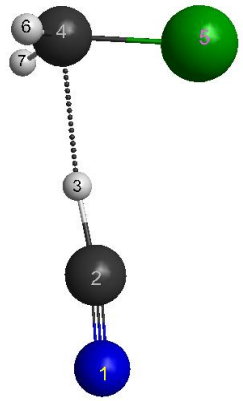


1	C						
2	Y	1	r_1				
3	H	1	r_2	2	a_1		
4	H	1	r_2	2	a_1	3	120.0
5	H	1	r_2	2	a_1	3	−120.0
6	C	1	r_3	3	180.0−a_1	2	180.0
7	Q	6	1	1	90.0	3	0
8	N	6	r_4	7	90.0	3	180.0

Level[a]	MP2/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVTZ			
System	**[F·CH$_3$·CN]$^-$**	**[Cl·CH$_3$·CN]$^-$**	**[Br·CH$_3$·CN]$^-$**	**[I·CH$_3$·CN]$^-$**	**[F·CH$_3$·CN]$^-$**	**[Cl·CH$_3$·CN]$^-$**	**[Br·CH$_3$·CN]$^-$**	**[I·CH$_3$·CN]$^-$**	**[F·CH$_3$·CN]$^-$**	**[Cl·CH$_3$·CN]$^-$**	**[Br·CH$_3$·CN]$^-$**	**[I·CH$_3$·CN]$^-$**
Energy [E_h]	−232.023364	−592.048279	−548.016638	−427.164542	−232.292498	−592.290391	−548.257154	−427.400271	−232.329863	−592.337679	−548.306546	−427.440363
r_1 [Å]	1.817	2.175	2.294	2.470	1.821	2.183	2.299	2.474	1.820	2.180	2.296	2.472
r_2 [Å]	1.083	1.083	1.083	1.084	1.073	1.073	1.073	1.074	1.071	1.071	1.072	1.072
r_3 [Å]	2.064	2.244	2.285	2.332	2.052	2.236	2.288	2.340	2.054	2.238	2.290	2.341
r_4 [Å]	1.200	1.202	1.202	1.203	1.173	1.174	1.174	1.175	1.173	1.174	1.175	1.175
a_1 [deg]	91.1	94.8	95.7	96.7	90.5	94.4	95.4	96.4	90.6	94.5	95.5	96.5
ZPE [cm^{-1}]	9758	9479	9352	9228	9732	9447	9346	9242	9759	9481	9364	9237
ω_1 [cm^{-1}]	650*i*	539*i*	490*i*	444*i*	662*i*	543*i*	481*i*	434*i*	660*i*	536*i*	474*i*	429*i*
ω_2 [cm^{-1}]	105	76	67	58	107	68	70	66	112	82	73	63
ω_3 [cm^{-1}]	105	76	68	58	108	72	71	67	113	82	74	63
ω_4 [cm^{-1}]	332	253	212	194	322	247	205	186	323	249	207	185
ω_5 [cm^{-1}]	392	296	269	241	383	289	265	237	391	296	267	237
ω_6 [cm^{-1}]	392	296	269	241	383	289	267	237	391	296	267	238
ω_7 [cm^{-1}]	1123	1027	989	947	1104	1001	965	927	1110	1007	970	924
ω_8 [cm^{-1}]	1123	1027	989	947	1104	1001	965	927	1111	1007	970	924
ω_9 [cm^{-1}]	1171	1081	1040	997	1156	1062	1026	988	1155	1065	1031	992
ω_{10} [cm^{-1}]	1390	1399	1399	1398	1389	1400	1403	1409	1394	1406	1409	1410
ω_{11} [cm^{-1}]	1390	1399	1399	1398	1389	1401	1404	1409	1394	1406	1409	1411
ω_{12} [cm^{-1}]	1994	1979	1975	1971	2131	2118	2114	2111	2126	2114	2110	2107
ω_{13} [cm^{-1}]	3191	3208	3203	3197	3167	3186	3182	3180	3170	3188	3186	3180
ω_{14} [cm^{-1}]	3404	3420	3413	3404	3361	3381	3376	3370	3364	3382	3378	3370
ω_{15} [cm^{-1}]	3404	3420	3413	3404	3362	3381	3376	3370	3364	3382	3378	3370

[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 DITS [Y = F, Cl, Br, I] double-inversion transition states (C_s symmetry) obtained at different levels of theory

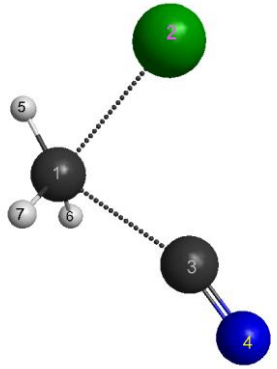


1	N						
2	C	1	r_1				
3	H	2	r_2	1	a_1		
4	C	3	r_3	2	a_2	1	180.0
5	Y	4	r_4	3	a_3	2	0.0
6	H	4	r_5	5	a_4	3	d_1
7	H	4	r_5	5	a_4	3	$-d_1$

Level[a]	MP2/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVTZ			
System	**[FCH$_2$···HCN]$^-$**	**[ClCH$_2$···HCN]$^-$**	**[BrCH$_2$···HCN]$^-$**	**[ICH$_2$···HCN]$^-$**	**[FCH$_2$···HCN]$^-$**	**[ClCH$_2$···HCN]$^-$**	**[BrCH$_2$···HCN]$^-$**	**[ICH$_2$···HCN]$^-$**	**[FCH$_2$···HCN]$^-$**	**[ClCH$_2$···HCN]$^-$**	**[BrCH$_2$···HCN]$^-$**	**[ICH$_2$···HCN]$^-$**
Energy [E_h]	−231.956425	−591.985726	−547.953692	−427.104427	−232.229205	−592.229735	−548.193119	−427.339677	−232.266015	−592.276291	−548.242248	−427.379999
r_1 [Å]	1.192	1.190	1.190	1.189	1.163	1.162	1.162	1.161	1.163	1.162	1.162	1.161
r_2 [Å]	1.201	1.169	1.166	1.157	1.168	1.145	1.145	1.137	1.164	1.144	1.142	1.134
r_3 [Å]	1.771	1.878	1.900	1.950	1.837	1.930	1.950	2.000	1.845	1.932	1.956	2.009
r_4 [Å]	1.449	1.795	1.931	2.112	1.426	1.768	1.922	2.094	1.427	1.774	1.924	2.095
r_5 [Å]	1.087	1.087	1.088	1.089	1.078	1.078	1.078	1.078	1.076	1.076	1.076	1.077
a_1 [deg]	168.8	170.9	171.7	173.4	171.4	172.4	173.5	174.7	171.3	172.5	173.3	174.5
a_2 [deg]	168.5	175.7	178.4	178.0	166.1	174.2	177.9	178.2	166.2	175.1	177.9	178.2
a_3 [deg]	81.4	83.5	84.8	87.4	79.3	82.2	84.2	87.1	78.9	82.1	83.9	86.9
a_4 [deg]	113.8	114.5	114.9	115.4	114.4	115.6	115.2	115.7	114.4	115.5	115.1	115.7
d_1 [deg]	79.6	79.0	79.4	79.6	81.7	80.1	81.1	81.0	82.1	80.8	81.4	81.3
ZPE [cm^{-1}]	8464	8440	8352	8303	8569	8525	8435	8380	8594	8522	8412	8361
ω_1 [cm^{-1}]	1012*i*	827*i*	824*i*	798*i*	999*i*	814*i*	846*i*	808*i*	998*i*	826*i*	855*i*	816*i*
ω_2 [cm^{-1}]	89	86	73	65	91	86	68	60	93	86	72	63
ω_3 [cm^{-1}]	131	149	150	151	143	153	162	157	152	160	153	152
ω_4 [cm^{-1}]	193	189	179	169	195	200	190	180	198	198	188	178
ω_5 [cm^{-1}]	260	250	242	228	243	243	235	224	246	246	233	222
ω_6 [cm^{-1}]	352	362	359	350	313	324	346	332	325	341	332	321
ω_7 [cm^{-1}]	920	729	635	585	937	727	621	576	931	721	617	573
ω_8 [cm^{-1}]	1072	966	915	859	1071	970	910	851	1071	966	904	845
ω_9 [cm^{-1}]	1125	1068	1059	1050	1108	1057	1054	1039	1105	1050	1046	1035
ω_{10} [cm^{-1}]	1149	1112	1112	1099	1122	1080	1084	1071	1110	1069	1067	1051
ω_{11} [cm^{-1}]	1403	1363	1339	1316	1401	1371	1328	1306	1402	1359	1321	1299
ω_{12} [cm^{-1}]	1481	1716	1731	1775	1666	1871	1873	1921	1691	1871	1881	1928
ω_{13} [cm^{-1}]	2173	2328	2349	2414	2354	2492	2499	2563	2360	2490	2505	2573
ω_{14} [cm^{-1}]	3204	3201	3199	3191	3164	3164	3170	3162	3170	3169	3172	3163
ω_{15} [cm^{-1}]	3377	3361	3363	3353	3328	3312	3330	3318	3333	3320	3333	3320

[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 FSTS [Y = Cl, Br, I] front-side attack transition states (C_s symmetry) obtained at different levels of theory

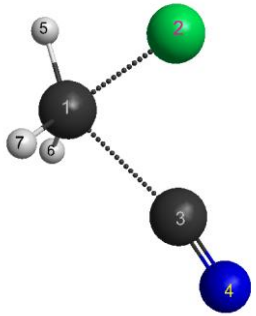


1	C						
2	Y	1	r_1				
3	C	1	r_2	2	a_1		
4	N	3	r_3	1	a_2	2	180.0
5	H	1	r_4	2	a_3	3	180.0
6	H	1	r_5	3	a_4	2	d_1
7	H	1	r_5	3	a_4	2	$-d_1$

Level[a]	MP2/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVTZ		
System	**[Cl···CH$_3$···CN]$^-$**	**[Br···CH$_3$···CN]$^-$**	**[I···CH$_3$···CN]$^-$**	**[Cl···CH$_3$···CN]$^-$**	**[Br···CH$_3$···CN]$^-$**	**[I···CH$_3$···CN]$^-$**	**[Cl···CH$_3$···CN]$^-$**	**[Br···CH$_3$···CN]$^-$**	**[I···CH$_3$···CN]$^-$**
Energy [E_h]	−591.970938	−547.941014	−427.090216	−592.215326	−548.183904	−427.329017	−592.262523	−548.233513	−427.369511
r_1 [Å]	2.326	2.482	2.715	2.374	2.548	2.795	2.374	2.543	2.795
r_2 [Å]	2.170	2.190	2.220	2.218	2.255	2.299	2.219	2.254	2.299
r_3 [Å]	1.203	1.203	1.204	1.175	1.175	1.175	1.175	1.175	1.175
r_4 [Å]	1.097	1.096	1.094	1.082	1.081	1.079	1.081	1.080	1.078
r_5 [Å]	1.092	1.091	1.091	1.080	1.080	1.079	1.079	1.078	1.078
a_1 [deg]	82.6	83.4	84.5	82.2	83.3	84.6	82.4	83.4	84.7
a_2 [deg]	160.6	159.4	159.9	160.7	159.9	159.6	160.4	159.6	159.3
a_3 [deg]	73.1	72.4	71.2	70.8	69.4	67.5	70.6	69.3	67.5
a_4 [deg]	80.9	80.5	80.0	79.6	78.7	77.8	79.5	78.7	77.8
d_1 [deg]	122.3	122.0	121.7	121.5	120.9	120.2	121.5	120.9	120.3
ZPE [cm^{-1}]	9196	9119	9026	9158	9074	8981	9163	9077	8965
ω_1 [cm^{-1}]	734*i*	711*i*	719*i*	712*i*	683*i*	689*i*	709*i*	682*i*	687*i*
ω_2 [cm^{-1}]	44	43	11	41*i*	47	18	93*i*	44*i*	77*i*
ω_3 [cm^{-1}]	74	62	47	81	68	50	81	68	45
ω_4 [cm^{-1}]	103	108	108	103	99	86	100	95	75
ω_5 [cm^{-1}]	229	198	179	208	178	159	208	179	159
ω_6 [cm^{-1}]	460	430	396	437	401	364	436	402	363
ω_7 [cm^{-1}]	896	876	834	854	816	751	854	817	752
ω_8 [cm^{-1}]	931	884	850	868	828	791	874	828	790
ω_9 [cm^{-1}]	1195	1165	1128	1152	1114	1070	1159	1122	1077
ω_{10} [cm^{-1}]	1431	1428	1425	1437	1434	1429	1440	1437	1431
ω_{11} [cm^{-1}]	1499	1494	1490	1494	1483	1475	1493	1486	1476
ω_{12} [cm^{-1}]	1960	1955	1949	2098	2097	2095	2094	2093	2091
ω_{13} [cm^{-1}]	3090	3100	3117	3105	3118	3130	3106	3117	3128
ω_{14} [cm^{-1}]	3205	3215	3232	3216	3237	3259	3219	3237	3258
ω_{15} [cm^{-1}]	3275	3280	3286	3260	3274	3285	3262	3274	3286

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

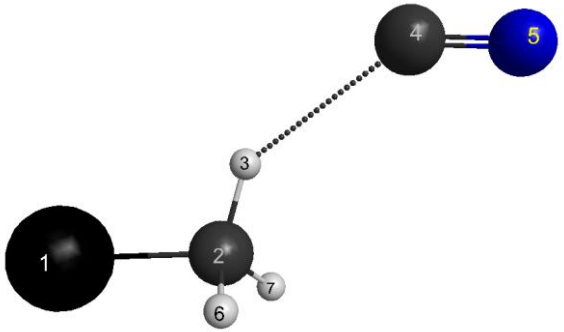
Table S8. Energies, structures, and frequencies for the FSTS [Y = F] front-side attack transition states (C_1 symmetry) obtained at different levels of theory



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

Level	**MP2/aug-cc-pVDZ**	**CCSD(T)-F12b/aug-cc-pVDZ**	**CCSD(T)-F12b/aug-cc-pVTZ**
Energy [E_h]	−231.952746	−232.222624	−232.259936
r_1 [Å]	1.769	1.784	1.787
r_2 [Å]	2.007	2.028	2.031
r_3 [Å]	1.201	1.174	1.174
r_4 [Å]	1.115	1.100	1.097
r_5 [Å]	1.104	1.093	1.091
r_6 [Å]	1.095	1.084	1.082
a_1 [deg]	78.4	78.0	78.1
a_2 [deg]	165.1	165.5	165.2
a_3 [deg]	78.8	78.1	78.0
a_4 [deg]	81.8	80.7	80.5
a_5 [deg]	92.3	93.3	93.1
d_1 [deg]	195.6	191.1	191.3
d_2 [deg]	196.0	199.4	199.2
d_3 [deg]	143.9	147.2	147.0
d_4 [deg]	−107.6	−103.8	−103.9
ZPE [cm^{-1}]	9442	9504	9520
ω_1 [cm^{-1}]	738*i*	156*i*	752*i*
ω_2 [cm^{-1}]	113	127	124
ω_3 [cm^{-1}]	120	144	139
ω_4 [cm^{-1}]	203	222	228
ω_5 [cm^{-1}]	367	344	342
ω_6 [cm^{-1}]	573	549	549
ω_7 [cm^{-1}]	977	969	969
ω_8 [cm^{-1}]	1118	1108	1108
ω_9 [cm^{-1}]	1313	1303	1309
ω_{10} [cm^{-1}]	1436	1445	1451
ω_{11} [cm^{-1}]	1543	1546	1550
ω_{12} [cm^{-1}]	1978	2108	2103
ω_{13} [cm^{-1}]	2910	2940	2948
ω_{14} [cm^{-1}]	3036	3020	3031
ω_{15} [cm^{-1}]	3197	3184	3189

Table S9. Energies, structures, and frequencies for the HTS2 [Y = I] H-bonded transition states (C_s symmetry) obtained at different levels of theory

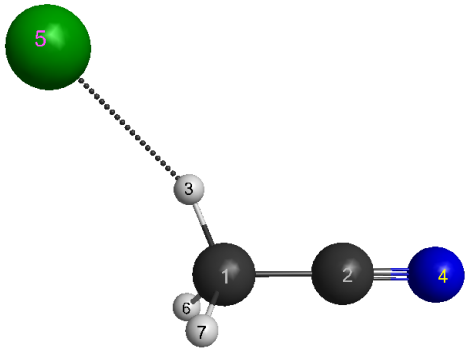


1	Y						
2	C	1	r_1				
3	H	2	r_2	1	a_1		
4	C	3	r_3	2	a_2	1	180.0
5	N	4	r_4	3	a_3	2	0.0
6	H	2	r_5	1	a_4	3	d_1
7	H	2	r_5	1	a_4	3	$-d_1$

Level[a]	**MP2/aug-cc-pVDZ**	**CCSD(T)-F12b/aug-cc-pVDZ**	**CCSD(T)-F12b/aug-cc-pVTZ**
Energy [E_h]	−427.170572	−427.406481	−427.446201
r_1 [Å]	2.172	2.158	2.159
r_2 [Å]	1.103	1.090	1.089
r_3 [Å]	2.264	2.329	2.324
r_4 [Å]	1.206	1.179	1.179
r_5 [Å]	1.096	1.086	1.084
a_1 [deg]	109.3	109.7	109.5
a_2 [deg]	151.3	140.5	141.4
a_3 [deg]	165.5	137.9	140.5
a_4 [deg]	106.5	106.6	106.4
d_1 [deg]	120.6	120.4	120.5
ZPE [cm^{-1}]	9187	9207	9213
ω_1 [cm^{-1}]	30*i*	37*i*	33*i*
ω_2 [cm^{-1}]	28	26	28
ω_3 [cm^{-1}]	39	29	35
ω_4 [cm^{-1}]	163	149	150
ω_5 [cm^{-1}]	187	150	150
ω_6 [cm^{-1}]	529	522	520
ω_7 [cm^{-1}]	901	885	888
ω_8 [cm^{-1}]	916	910	909
ω_9 [cm^{-1}]	1291	1290	1293
ω_{10} [cm^{-1}]	1444	1461	1465
ω_{11} [cm^{-1}]	1471	1485	1490
ω_{12} [cm^{-1}]	1949	2079	2075
ω_{13} [cm^{-1}]	3039	3052	3048
ω_{14} [cm^{-1}]	3189	3175	3173
ω_{15} [cm^{-1}]	3229	3201	3203

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

Table S10. Energies, structures, and frequencies for the PostHMIN2 [Y = F, Cl, Br, I] H-bonded complexes (C_s symmetry) obtained at different levels of theory

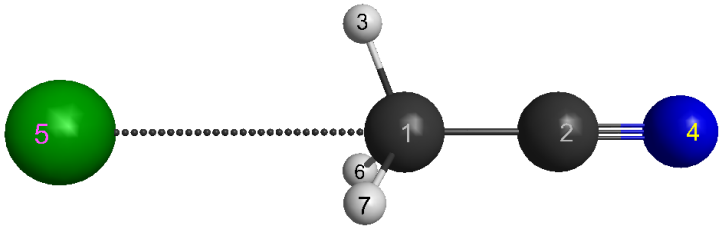


1	C						
2	C	1	r_1				
3	H	1	r_2	2	a_1		
4	N	2	r_3	1	a_2	3	0.0
5	Y	3	r_4	1	a_3	2	180.0
6	H	1	r_5	2	a_4	3	d_1
7	H	1	r_5	2	a_4	3	$-d_1$

Level[a]	**MP2/aug-cc-pVDZ**				**CCSD(T)-F12b/aug-cc-pVDZ**			**CCSD(T)-F12b/aug-cc-pVTZ**		
System	**F^-···CH_3CN**	**Cl^-···CH_3CN**	**Br^-···CH_3CN**	**I^-···CH_3CN**	**F^-···CH_3CN**	**Cl^-···CH_3CN**	**Br^-···CH_3CN**	**F^-···CH_3CN**	**Cl^-···CH_3CN**	**Br^-···CH_3CN**
Energy [E_h]	−232.087315	−592.129206	−548.100883	−427.253228	−232.352791	−592.366759	−548.337614	−232.390196	−592.414231	−548.387173
r_1 [Å]	1.463	1.469	1.469	1.470	1.456	1.462	1.462	1.454	1.461	1.461
r_2 [Å]	1.175	1.111	1.108	1.103	1.167	1.102	1.097	1.166	1.100	1.096
r_3 [Å]	1.190	1.187	1.187	1.187	1.163	1.160	1.160	1.163	1.160	1.160
r_4 [Å]	1.503	2.338	2.531	2.861	1.489	2.333	2.564	1.489	2.335	2.564
r_5 [Å]	1.102	1.099	1.100	1.099	1.093	1.091	1.091	1.092	1.089	1.089
a_1 [deg]	113.5	112.8	112.7	112.4	113.5	113.0	112.9	113.5	113.0	112.9
a_2 [deg]	179.8	181.0	181.0	180.5	180.0	181.0	180.9	180.0	181.0	180.9
a_3 [deg]	172.2	157.6	153.6	140.3	172.0	154.3	146.5	172.2	153.5	146.5
a_4 [deg]	108.7	109.3	109.5	109.9	108.6	109.4	109.6	108.7	109.4	109.6
d_1 [deg]	121.0	120.4	120.3	120.0	121.0	120.3	120.2	121.0	120.3	120.2
ZPE [cm^{-1}]	9680	9926	9911	9874	9725	9979	9956	9738	9985	9966
ω_1 [cm^{-1}]	98	50	39	2	98	47	22	98	47	34
ω_2 [cm^{-1}]	296	149	118	88	293	145	110	293	147	109
ω_3 [cm^{-1}]	309	176	153	106	310	166	132	309	155	122
ω_4 [cm^{-1}]	403	375	373	366	413	384	379	412	383	381
ω_5 [cm^{-1}]	431	380	375	370	443	389	382	443	389	382
ω_6 [cm^{-1}]	936	927	927	925	927	919	918	928	919	918
ω_7 [cm^{-1}]	1004	1016	1015	1009	1017	1026	1023	1021	1030	1028
ω_8 [cm^{-1}]	1084	1055	1051	1044	1096	1067	1060	1100	1068	1063
ω_9 [cm^{-1}]	1419	1390	1385	1372	1441	1409	1402	1446	1413	1406
ω_{10} [cm^{-1}]	1451	1448	1447	1446	1469	1464	1466	1472	1468	1468
ω_{11} [cm^{-1}]	1487	1464	1459	1453	1504	1483	1476	1511	1486	1481
ω_{12} [cm^{-1}]	2057	2165	2166	2167	2018	2288	2290	2016	2283	2286
ω_{13} [cm^{-1}]	2158	2957	3002	3060	2268	2943	3004	2264	2943	3001
ω_{14} [cm^{-1}]	3083	3124	3132	3154	3051	3092	3106	3055	3096	3106
ω_{15} [cm^{-1}]	3145	3176	3179	3187	3103	3137	3144	3107	3141	3146

[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 S11. Energies, structures, and frequencies for the WaldenPostMIN [Y = Cl, Br, I] ion-dipole complexes (C_{3v} symmetry)[a] obtained at different levels of theory



1	C						
2	C	1	r_1				
3	H	1	r_2	2	a_1		
4	N	2	r_3	1	a_2	3	0.0
5	Y	1	r_4	3	a_3	2	180.0
6	H	1	r_5	2	a_4	3	d_1
7	H	1	r_5	2	a_4	3	$-d_1$

Level[b]	**MP2/aug-cc-pVDZ**			**CCSD(T)-F12b/aug-cc-pVDZ**			**CCSD(T)-F12b/aug-cc-pVTZ**		
System	**$Cl^-\cdots CH_3CN$**	**$Br^-\cdots CH_3CN$**	**$I^-\cdots CH_3CN$**	**$Cl^-\cdots CH_3CN$**	**$Br^-\cdots CH_3CN$**	**$I^-\cdots CH_3CN$**	**$Cl^-\cdots CH_3CN$**	**$Br^-\cdots CH_3CN$**	**$I^-\cdots CH_3CN$**
Energy [E_h]	−592.128793	−548.100913	−427.253603	−592.366431	−548.337748	−427.485942	−592.413861	−548.387304	−427.526543
r_1 [Å]	1.473	1.473	1.472	1.465	1.465	1.465	1.464	1.464	1.464
r_2 [Å]	1.097	1.097	1.098	1.088	1.089	1.089	1.087	1.087	1.087
r_3 [Å]	1.187	1.187	1.187	1.160	1.160	1.160	1.160	1.160	1.160
r_4 [Å]	3.226	3.395	3.633	3.204	3.375	3.624	3.205	3.385	3.644
r_5 [Å]	1.097	1.097	1.098	1.088	1.089	1.089	1.087	1.087	1.087
a_1 [deg]	111.4	111.2	111.1	111.4	111.2	111.1	111.4	111.2	111.0
a_2 [deg]	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0
a_3 [deg]	68.6	69.0	69.2	68.6	69.0	69.2	68.6	69.0	69.2
a_4 [deg]	111.4	111.3	111.2	111.4	111.3	111.1	111.4	111.3	111.0
d_1 [deg]	120.0	120.0	119.9	120.0	120.0	120.0	120.0	120.0	120.0
ZPE [cm^{-1}]	9876	9872	9871	9874	9911	9931	9941	9938	9940
ω_1 [cm^{-1}]	38	39	39	29*i*	26	37	30	34	35
ω_2 [cm^{-1}]	38	39	39	29*i*	27	37	34	36	36
ω_3 [cm^{-1}]	120	93	79	119	97	79	119	92	77
ω_4 [cm^{-1}]	371	370	369	361	370	376	378	378	377
ω_5 [cm^{-1}]	371	370	369	361	370	376	379	378	377
ω_6 [cm^{-1}]	913	314	916	904	906	907	905	907	908
ω_7 [cm^{-1}]	1005	1009	1014	1011	1021	1028	1021	1025	1031
ω_8 [cm^{-1}]	1005	1010	1014	1011	1021	1028	1021	1026	1032
ω_9 [cm^{-1}]	1335	1341	1348	1359	1367	1374	1364	1372	1381
ω_{10} [cm^{-1}]	1432	1435	1439	1453	1455	1459	1458	1461	1465
ω_{11} [cm^{-1}]	1432	1435	1439	1453	1455	1460	1458	1461	1465
ω_{12} [cm^{-1}]	2162	2164	2166	2287	2289	2291	2282	2284	2287
ω_{13} [cm^{-1}]	3113	3110	3106	3090	3085	3082	3090	3086	3081
ω_{14} [cm^{-1}]	3208	3206	3202	3170	3166	3164	3171	3167	3164
ω_{15} [cm^{-1}]	3208	3207	3203	3170	3167	3164	3171	3168	3164

[a] The computations are performed using C_s symmetry, but the C_{3v} symmetry, with collinear Y(5), C(1), C(2), N(4) atoms, is numerically obtained.
[b] For Br and I effective core potentials and the corresponding aug-cc-pVDZ-PP and aug-cc-pVTZ-PP basis sets are employed.