

# ELECTRONIC SUPPLEMENTARY INFORMATION

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

**Domonkos A. Tasi, Zita Fábrián, and Gábor Czako\***

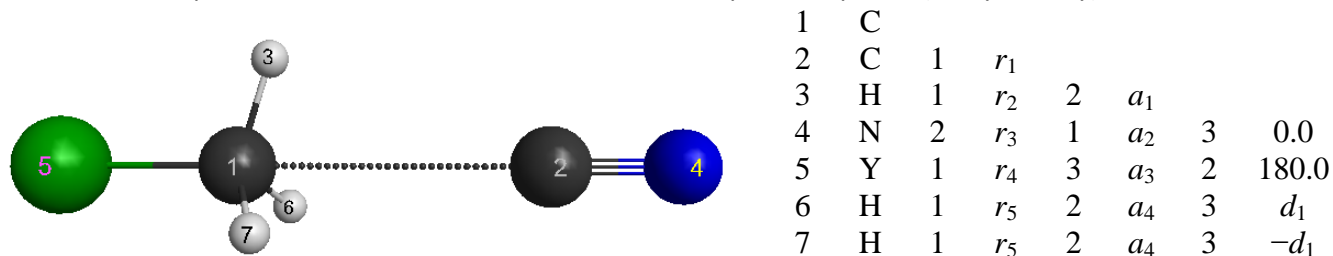
Interdisciplinary Excellence Centre and Department of Physical Chemistry and Materials Science,  
Institute of Chemistry, University of Szeged, Rerrich Béla tér 1, Szeged H-6720, Hungary

\* gczako@chem.u-szeged.hu

### Content

Energies, structures, and frequencies for the stationary points of the potential energy surface of the  $CN^- + CH_3Y$  [ $Y = F, Cl, Br, I$ ]  $S_N2$  reactions obtained at different levels of theory

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

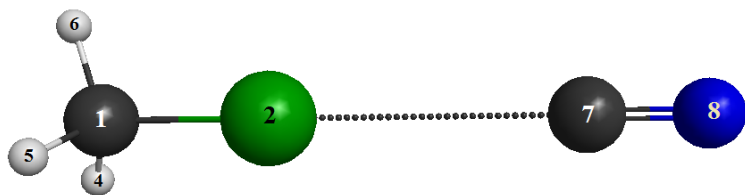


Level <sup>b</sup>	MP2/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVTZ			
	FCH <sub>3</sub> ...CN <sup>-</sup>	ClCH <sub>3</sub> ...CN <sup>-</sup>	BrCH <sub>3</sub> ...CN <sup>-</sup>	ICH <sub>3</sub> ...CN <sup>-</sup>	FCH <sub>3</sub> ...CN <sup>-</sup>	ClCH <sub>3</sub> ...CN <sup>-</sup>	BrCH <sub>3</sub> ...CN <sup>-</sup>	ICH <sub>3</sub> ...CN <sup>-</sup>	FCH <sub>3</sub> ...CN <sup>-</sup>	ClCH <sub>3</sub> ...CN <sup>-</sup>	BrCH <sub>3</sub> ...CN <sup>-</sup>	ICH <sub>3</sub> ...CN <sup>-</sup>
Energy [E <sub>h</sub> ]	-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 <sup>-1</sup> ]	9803	9431	9281	9136	9838	9469	9357	9189	9846	9470	9329	9178
$\omega_1$ [cm <sup>-1</sup> ]	28	23	23	18	31	35	39	31	31	23	26	20
$\omega_2$ [cm <sup>-1</sup> ]	28	23	23	18	31	36	42	31	32	25	26	21
$\omega_3$ [cm <sup>-1</sup> ]	115	101	95	87	113	87	95	85	112	90	91	83
$\omega_4$ [cm <sup>-1</sup> ]	129	101	95	87	118	88	106	85	122	93	92	84
$\omega_5$ [cm <sup>-1</sup> ]	129	111	103	100	119	109	108	99	123	108	102	97
$\omega_6$ [cm <sup>-1</sup> ]	937	652	542	472	987	658	538	468	980	657	534	463
$\omega_7$ [cm <sup>-1</sup> ]	1146	999	939	876	1163	1007	942	873	1162	999	936	870
$\omega_8$ [cm <sup>-1</sup> ]	1146	999	939	876	1163	1007	943	873	1162	999	937	870
$\omega_9$ [cm <sup>-1</sup> ]	1409	1304	1258	1208	1429	1326	1271	1221	1431	1329	1273	1221
$\omega_{10}$ [cm <sup>-1</sup> ]	1474	1448	1439	1430	1489	1469	1462	1452	1494	1475	1465	1456
$\omega_{11}$ [cm <sup>-1</sup> ]	1474	1448	1439	1431	1490	1469	1463	1452	1494	1476	1466	1456
$\omega_{12}$ [cm <sup>-1</sup> ]	1952	1952	1952	1952	2079	2080	2082	2082	2076	2077	2078	2078
$\omega_{13}$ [cm <sup>-1</sup> ]	3128	3144	3145	3144	3084	3114	3124	3124	3087	3119	3126	3126
$\omega_{14}$ [cm <sup>-1</sup> ]	3257	3279	3285	3287	3189	3227	3249	3251	3193	3235	3252	3255
$\omega_{15}$ [cm <sup>-1</sup> ]	3257	3279	3285	3287	3189	3228	3249	3251	3193	3235	3252	3255

<sup>a</sup> 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.

<sup>b</sup> 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

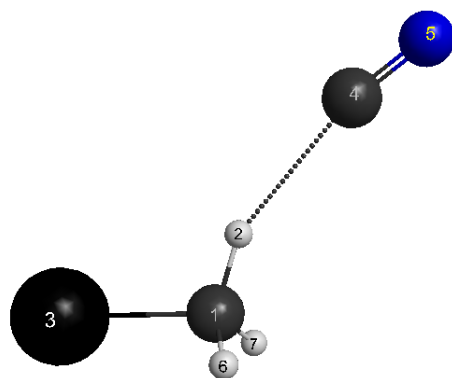


1	C								
2	Y	1	$r_1$						
3	Q	2	1.0	1	90.0				
4	H	1	$r_2$	2	$a_1$	3	0.0		
5	H	1	$r_2$	2	$a_1$	4	120.0		
6	H	1	$r_2$	2	$a_1$	4	-120.0		
7	C	2	$r_3$	3	90.0	1	180.0		
8	N	2	$r_4$	3	90.0	1	180.0		

Level <sup>a</sup>	MP2/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVTZ		
	CH <sub>3</sub> Cl...CN <sup>-</sup>	CH <sub>3</sub> Br...CN <sup>-</sup>	CH <sub>3</sub> I...CN <sup>-</sup>	CH <sub>3</sub> Cl...CN <sup>-</sup>	CH <sub>3</sub> Br...CN <sup>-</sup>	CH <sub>3</sub> I...CN <sup>-</sup>	CH <sub>3</sub> Cl...CN <sup>-</sup>	CH <sub>3</sub> Br...CN <sup>-</sup>	CH <sub>3</sub> I...CN <sup>-</sup>
Energy [E <sub>h</sub> ]	-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 <sup>-1</sup> ]	9386	9272	9129	9418	9338	9185	9454	9333	9181
$\omega_1$ [cm <sup>-1</sup> ]	24	50	68	35	52	72	35	55	68
$\omega_2$ [cm <sup>-1</sup> ]	24	50	68	37	66	72	36	55	68
$\omega_3$ [cm <sup>-1</sup> ]	68	100	130	59	104	134	69	104	135
$\omega_4$ [cm <sup>-1</sup> ]	90	137	182	60	145	189	97	143	183
$\omega_5$ [cm <sup>-1</sup> ]	90	137	182	80	148	189	97	143	183
$\omega_6$ [cm <sup>-1</sup> ]	753	600	488	754	594	489	751	593	488
$\omega_7$ [cm <sup>-1</sup> ]	1018	929	819	1037	934	820	1025	931	819
$\omega_8$ [cm <sup>-1</sup> ]	1018	929	819	1037	936	820	1025	931	819
$\omega_9$ [cm <sup>-1</sup> ]	1354	1292	1216	1375	1304	1228	1378	1304	1225
$\omega_{10}$ [cm <sup>-1</sup> ]	1472	1462	1452	1490	1482	1470	1497	1486	1475
$\omega_{11}$ [cm <sup>-1</sup> ]	1472	1462	1452	1491	1484	1471	1497	1486	1475
$\omega_{12}$ [cm <sup>-1</sup> ]	1947	1955	1969	2073	2084	2102	2069	2081	2098
$\omega_{13}$ [cm <sup>-1</sup> ]	3077	3074	3064	3045	3052	3041	3052	3054	3043
$\omega_{14}$ [cm <sup>-1</sup> ]	3183	3184	3175	3131	3146	3138	3140	3150	3141
$\omega_{15}$ [cm <sup>-1</sup> ]	3183	3184	3175	3131	3146	3138	3140	3150	3141

<sup>a</sup> 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

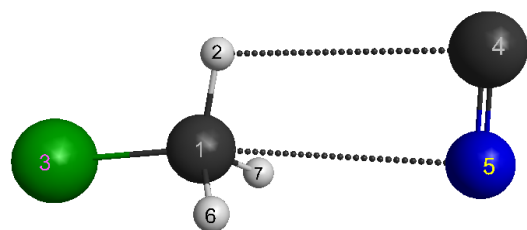


1	C							
2	H	1	$r_1$					
3	Y	1	$r_2$	2	$a_1$			
4	C	2	$r_3$	1	$a_2$	3	180.0	
5	N	4	$r_4$	2	$a_3$	1	0.0	
6	H	1	$r_5$	3	$a_4$	2	$d_1$	
7	H	1	$r_5$	3	$a_4$	2	$-d_1$	

Level <sup>a</sup>	MP2/aug-cc-pVDZ		CCSD(T)-F12b/aug-cc-pVDZ		CCSD(T)-F12b/aug-cc-pVTZ	
	BrCH <sub>3</sub> ...CN <sup>-</sup>	ICH <sub>3</sub> ...CN <sup>-</sup>	BrCH <sub>3</sub> ...CN <sup>-</sup>	ICH <sub>3</sub> ...CN <sup>-</sup>	BrCH <sub>3</sub> ...CN <sup>-</sup>	ICH <sub>3</sub> ...CN <sup>-</sup>
Energy [E <sub>h</sub> ]	-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 <sup>-1</sup> ]	9322	9231	9340	9276	9340	9255
$\omega_1$ [cm <sup>-1</sup> ]	16	28	8i	35	11i	35
$\omega_2$ [cm <sup>-1</sup> ]	37	46	38	56	35	44
$\omega_3$ [cm <sup>-1</sup> ]	44	58	46	69	37	56
$\omega_4$ [cm <sup>-1</sup> ]	143	160	126	153	129	152
$\omega_5$ [cm <sup>-1</sup> ]	187	217	159	196	148	180
$\omega_6$ [cm <sup>-1</sup> ]	594	531	588	527	584	523
$\omega_7$ [cm <sup>-1</sup> ]	953	919	940	914	942	909
$\omega_8$ [cm <sup>-1</sup> ]	980	921	977	918	976	915
$\omega_9$ [cm <sup>-1</sup> ]	1334	1305	1335	1311	1337	1308
$\omega_{10}$ [cm <sup>-1</sup> ]	1453	1447	1468	1463	1473	1466
$\omega_{11}$ [cm <sup>-1</sup> ]	1481	1481	1492	1497	1499	1499
$\omega_{12}$ [cm <sup>-1</sup> ]	1952	1954	2081	2084	2077	2080
$\omega_{13}$ [cm <sup>-1</sup> ]	3052	3001	3059	2994	3061	3000
$\omega_{14}$ [cm <sup>-1</sup> ]	3192	3174	3178	3146	3181	3150
$\omega_{15}$ [cm <sup>-1</sup> ]	3224	3221	3194	3188	3200	3193

<sup>a</sup> 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

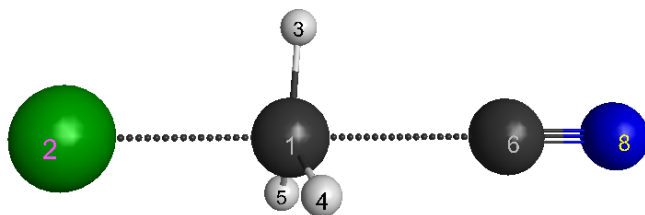


1	C											
2	H	1	$r_1$									
3	Y	1	$r_2$	2	$a_1$							
4	C	2	$r_3$	1	$a_2$	3	180.0					
5	N	4	$r_4$	2	$a_3$	1	0.0					
6	H	1	$r_5$	3	$a_4$	2	$d_1$					
7	H	1	$r_5$	3	$a_4$	2	$-d_1$					

Level <sup>a</sup>	MP2/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVTZ			
	FCH <sub>3</sub> ...CN <sup>-</sup>	ClCH <sub>3</sub> ...CN <sup>-</sup>	BrCH <sub>3</sub> ...CN <sup>-</sup>	ICH <sub>3</sub> ...CN <sup>-</sup>	FCH <sub>3</sub> ...CN <sup>-</sup>	ClCH <sub>3</sub> ...CN <sup>-</sup>	BrCH <sub>3</sub> ...CN <sup>-</sup>	ICH <sub>3</sub> ...CN <sup>-</sup>	FCH <sub>3</sub> ...CN <sup>-</sup>	ClCH <sub>3</sub> ...CN <sup>-</sup>	BrCH <sub>3</sub> ...CN <sup>-</sup>	ICH <sub>3</sub> ...CN <sup>-</sup>
<b>Energy [E<sub>h</sub>]</b>	-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
<b>ZPE [cm<sup>-1</sup>]</b>	9799	9446	9293	9154	9832	9454	9351	9199	9857	9478	9334	9203
$\omega_1$ [cm <sup>-1</sup> ]	12i	6	20i	31i	36i	42i	29	3	31	35i	33i	10
$\omega_2$ [cm <sup>-1</sup> ]	52	67	68	64	57	44	71	65	58	66	69	66
$\omega_3$ [cm <sup>-1</sup> ]	108	85	79	71	96	66	74	69	100	74	71	69
$\omega_4$ [cm <sup>-1</sup> ]	110	86	79	74	102	75	84	75	104	78	74	74
$\omega_5$ [cm <sup>-1</sup> ]	133	127	116	113	127	122	114	110	127	120	113	109
$\omega_6$ [cm <sup>-1</sup> ]	946	667	562	497	994	670	559	491	987	671	555	488
$\omega_7$ [cm <sup>-1</sup> ]	1149	1002	942	878	1166	1007	941	874	1166	1001	938	873
$\omega_8$ [cm <sup>-1</sup> ]	1151	1005	944	880	1169	1014	944	879	1169	1005	943	878
$\omega_9$ [cm <sup>-1</sup> ]	1425	1322	1279	1234	1445	1343	1292	1244	1446	1346	1294	1246
$\omega_{10}$ [cm <sup>-1</sup> ]	1474	1448	1439	1431	1490	1470	1462	1453	1495	1476	1466	1458
$\omega_{11}$ [cm <sup>-1</sup> ]	1479	1455	1446	1437	1495	1474	1465	1458	1499	1480	1470	1462
$\omega_{12}$ [cm <sup>-1</sup> ]	1943	1942	1941	1940	2070	2069	2069	2068	2067	2066	2065	2065
$\omega_{13}$ [cm <sup>-1</sup> ]	3123	3138	3138	3136	3081	3109	3118	3119	3084	3114	3120	3119
$\omega_{14}$ [cm <sup>-1</sup> ]	3252	3271	3276	3276	3186	3220	3238	3242	3190	3228	3243	3244
$\omega_{15}$ [cm <sup>-1</sup> ]	3252	3273	3278	3278	3186	3224	3242	3247	3191	3231	3247	3247

<sup>a</sup> 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

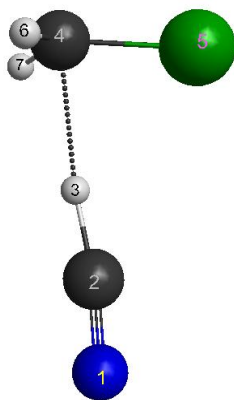


1	C											
2	Y	1	$r_1$									
3	H	1	$r_2$	2	$a_1$							
4	H	1	$r_2$	2	$a_1$	3	120.0					
5	H	1	$r_2$	2	$a_1$	3	-120.0					
6	C	1	$r_3$	3	$180.0 - a_1$	2	180.0					
7	Q	6	1	1	90.0	3	0					
8	N	6	$r_4$	7	90.0	3	180.0					

Level <sup>a</sup>	MP2/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVTZ			
	[F-CH <sub>3</sub> CN] <sup>-</sup>	[Cl-CH <sub>3</sub> CN] <sup>-</sup>	[Br-CH <sub>3</sub> CN] <sup>-</sup>	[I-CH <sub>3</sub> CN] <sup>-</sup>	[F-CH <sub>3</sub> CN] <sup>-</sup>	[Cl-CH <sub>3</sub> CN] <sup>-</sup>	[Br-CH <sub>3</sub> CN] <sup>-</sup>	[I-CH <sub>3</sub> CN] <sup>-</sup>	[F-CH <sub>3</sub> CN] <sup>-</sup>	[Cl-CH <sub>3</sub> CN] <sup>-</sup>	[Br-CH <sub>3</sub> CN] <sup>-</sup>	[I-CH <sub>3</sub> CN] <sup>-</sup>
Energy [E <sub>h</sub> ]	-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 <sup>-1</sup> ]	9758	9479	9352	9228	9732	9447	9346	9242	9759	9481	9364	9237
$\omega_1$ [cm <sup>-1</sup> ]	650i	539i	490i	444i	662i	543i	481i	434i	660i	536i	474i	429i
$\omega_2$ [cm <sup>-1</sup> ]	105	76	67	58	107	68	70	66	112	82	73	63
$\omega_3$ [cm <sup>-1</sup> ]	105	76	68	58	108	72	71	67	113	82	74	63
$\omega_4$ [cm <sup>-1</sup> ]	332	253	212	194	322	247	205	186	323	249	207	185
$\omega_5$ [cm <sup>-1</sup> ]	392	296	269	241	383	289	265	237	391	296	267	237
$\omega_6$ [cm <sup>-1</sup> ]	392	296	269	241	383	289	267	237	391	296	267	238
$\omega_7$ [cm <sup>-1</sup> ]	1123	1027	989	947	1104	1001	965	927	1110	1007	970	924
$\omega_8$ [cm <sup>-1</sup> ]	1123	1027	989	947	1104	1001	965	927	1111	1007	970	924
$\omega_9$ [cm <sup>-1</sup> ]	1171	1081	1040	997	1156	1062	1026	988	1155	1065	1031	992
$\omega_{10}$ [cm <sup>-1</sup> ]	1390	1399	1399	1398	1389	1400	1403	1409	1394	1406	1409	1410
$\omega_{11}$ [cm <sup>-1</sup> ]	1390	1399	1399	1398	1389	1401	1404	1409	1394	1406	1409	1411
$\omega_{12}$ [cm <sup>-1</sup> ]	1994	1979	1975	1971	2131	2118	2114	2111	2126	2114	2110	2107
$\omega_{13}$ [cm <sup>-1</sup> ]	3191	3208	3203	3197	3167	3186	3182	3180	3170	3188	3186	3180
$\omega_{14}$ [cm <sup>-1</sup> ]	3404	3420	3413	3404	3361	3381	3376	3370	3364	3382	3378	3370
$\omega_{15}$ [cm <sup>-1</sup> ]	3404	3420	3413	3404	3362	3381	3376	3370	3364	3382	3378	3370

<sup>a</sup> 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

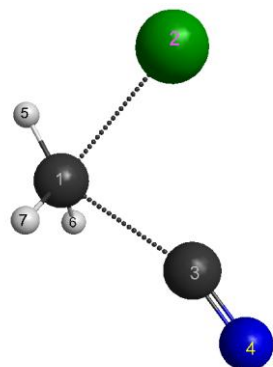


1	N										
2	C	1	$r_1$								
3	H	2	$r_2$	1	$a_1$						
4	C	3	$r_3$	2	$a_2$	1	180.0				
5	Y	4	$r_4$	3	$a_3$	2	0.0				
6	H	4	$r_5$	5	$a_4$	3	$d_1$				
7	H	4	$r_5$	5	$a_4$	3	$-d_1$				

Level <sup>a</sup>	MP2/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVTZ			
	[FCH <sub>2</sub> ...HCN] <sup>-</sup>	[ClCH <sub>2</sub> ...HCN] <sup>-</sup>	[BrCH <sub>2</sub> ...HCN] <sup>-</sup>	[ICH <sub>2</sub> ...HCN] <sup>-</sup>	[FCH <sub>2</sub> ...HCN] <sup>-</sup>	[ClCH <sub>2</sub> ...HCN] <sup>-</sup>	[BrCH <sub>2</sub> ...HCN] <sup>-</sup>	[ICH <sub>2</sub> ...HCN] <sup>-</sup>	[FCH <sub>2</sub> ...HCN] <sup>-</sup>	[ClCH <sub>2</sub> ...HCN] <sup>-</sup>	[BrCH <sub>2</sub> ...HCN] <sup>-</sup>	[ICH <sub>2</sub> ...HCN] <sup>-</sup>
Energy [E <sub>h</sub> ]	-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	1.162	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 <sup>-1</sup> ]	8464	8440	8352	8303	8569	8525	8435	8380	8594	8522	8412	8361
$\omega_1$ [cm <sup>-1</sup> ]	1012i	827i	824i	798i	999i	814i	846i	808i	998i	826i	855i	816i
$\omega_2$ [cm <sup>-1</sup> ]	89	86	73	65	91	86	68	60	93	86	72	63
$\omega_3$ [cm <sup>-1</sup> ]	131	149	150	151	143	153	162	157	152	160	153	152
$\omega_4$ [cm <sup>-1</sup> ]	193	189	179	169	195	200	190	180	198	198	188	178
$\omega_5$ [cm <sup>-1</sup> ]	260	250	242	228	243	243	235	224	246	246	233	222
$\omega_6$ [cm <sup>-1</sup> ]	352	362	359	350	313	324	346	332	325	341	332	321
$\omega_7$ [cm <sup>-1</sup> ]	920	729	635	585	937	727	621	576	931	721	617	573
$\omega_8$ [cm <sup>-1</sup> ]	1072	966	915	859	1071	970	910	851	1071	966	904	845
$\omega_9$ [cm <sup>-1</sup> ]	1125	1068	1059	1050	1108	1057	1054	1039	1105	1050	1046	1035
$\omega_{10}$ [cm <sup>-1</sup> ]	1149	1112	1112	1099	1122	1080	1084	1071	1110	1069	1067	1051
$\omega_{11}$ [cm <sup>-1</sup> ]	1403	1363	1339	1316	1401	1371	1328	1306	1402	1359	1321	1299
$\omega_{12}$ [cm <sup>-1</sup> ]	1481	1716	1731	1775	1666	1871	1873	1921	1691	1871	1881	1928
$\omega_{13}$ [cm <sup>-1</sup> ]	2173	2328	2349	2414	2354	2492	2499	2563	2360	2490	2505	2573
$\omega_{14}$ [cm <sup>-1</sup> ]	3204	3201	3199	3191	3164	3164	3170	3162	3170	3169	3172	3163
$\omega_{15}$ [cm <sup>-1</sup> ]	3377	3361	3363	3353	3328	3312	3330	3318	3333	3320	3333	3320

<sup>a</sup> 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



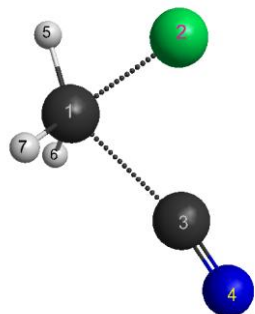
1	C								
2	Y	1	$r_1$						
3	C	1	$r_2$	2	$a_1$				
4	N	3	$r_3$	1	$a_2$	2	180.0		
5	H	1	$r_4$	2	$a_3$	3	180.0		
6	H	1	$r_5$	3	$a_4$	2	$d_1$		
7	H	1	$r_5$	3	$a_4$	2	$-d_1$		

Level <sup>a</sup>	MP2/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVTZ		
	[Cl...CH <sub>3</sub> ...CN] <sup>-</sup>	[Br...CH <sub>3</sub> ...CN] <sup>-</sup>	[I...CH <sub>3</sub> ...CN] <sup>-</sup>	[Cl...CH <sub>3</sub> ...CN] <sup>-</sup>	[Br...CH <sub>3</sub> ...CN] <sup>-</sup>	[I...CH <sub>3</sub> ...CN] <sup>-</sup>	[Cl...CH <sub>3</sub> ...CN] <sup>-</sup>	[Br...CH <sub>3</sub> ...CN] <sup>-</sup>	[I...CH <sub>3</sub> ...CN] <sup>-</sup>
<b>Energy [E<sub>h</sub>]</b>	-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
<b>ZPE [cm<sup>-1</sup>]</b>	9196	9119	9026	9158	9074	8981	9163	9077	8965
$\omega_1$ [cm <sup>-1</sup> ]	734i	711i	719i	712i	683i	689i	709i	682i	687i
$\omega_2$ [cm <sup>-1</sup> ]	44	43	11	41i	47	18	93i	44i	77i
$\omega_3$ [cm <sup>-1</sup> ]	74	62	47	81	68	50	81	68	45
$\omega_4$ [cm <sup>-1</sup> ]	103	108	108	103	99	86	100	95	75
$\omega_5$ [cm <sup>-1</sup> ]	229	198	179	208	178	159	208	179	159
$\omega_6$ [cm <sup>-1</sup> ]	460	430	396	437	401	364	436	402	363
$\omega_7$ [cm <sup>-1</sup> ]	896	876	834	854	816	751	854	817	752
$\omega_8$ [cm <sup>-1</sup> ]	931	884	850	868	828	791	874	828	790
$\omega_9$ [cm <sup>-1</sup> ]	1195	1165	1128	1152	1114	1070	1159	1122	1077
$\omega_{10}$ [cm <sup>-1</sup> ]	1431	1428	1425	1437	1434	1429	1440	1437	1431
$\omega_{11}$ [cm <sup>-1</sup> ]	1499	1494	1490	1494	1483	1475	1493	1486	1476
$\omega_{12}$ [cm <sup>-1</sup> ]	1960	1955	1949	2098	2097	2095	2094	2093	2091
$\omega_{13}$ [cm <sup>-1</sup> ]	3090	3100	3117	3105	3118	3130	3106	3117	3128
$\omega_{14}$ [cm <sup>-1</sup> ]	3205	3215	3232	3216	3237	3259	3219	3237	3258
$\omega_{15}$ [cm <sup>-1</sup> ]	3275	3280	3286	3260	3274	3285	3262	3274	3286

<sup>a</sup> For Br and I effective core potentials and the corresponding aug-cc-pVDZ-PP and aug-cc-pVTZ-PP basis sets are employed.



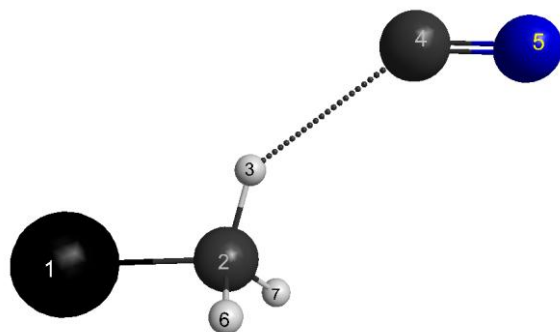
**Table S8.** Energies, structures, and frequencies for the FSTS [Y = F] front-side attack transition states ( $C_1$  symmetry) obtained at different levels of theory



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 [ $\text{cm}^{-1}$ ]	9442	9504	9520
$\omega_1$ [ $\text{cm}^{-1}$ ]	738i	156i	752i
$\omega_2$ [ $\text{cm}^{-1}$ ]	113	127	124
$\omega_3$ [ $\text{cm}^{-1}$ ]	120	144	139
$\omega_4$ [ $\text{cm}^{-1}$ ]	203	222	228
$\omega_5$ [ $\text{cm}^{-1}$ ]	367	344	342
$\omega_6$ [ $\text{cm}^{-1}$ ]	573	549	549
$\omega_7$ [ $\text{cm}^{-1}$ ]	977	969	969
$\omega_8$ [ $\text{cm}^{-1}$ ]	1118	1108	1108
$\omega_9$ [ $\text{cm}^{-1}$ ]	1313	1303	1309
$\omega_{10}$ [ $\text{cm}^{-1}$ ]	1436	1445	1451
$\omega_{11}$ [ $\text{cm}^{-1}$ ]	1543	1546	1550
$\omega_{12}$ [ $\text{cm}^{-1}$ ]	1978	2108	2103
$\omega_{13}$ [ $\text{cm}^{-1}$ ]	2910	2940	2948
$\omega_{14}$ [ $\text{cm}^{-1}$ ]	3036	3020	3031
$\omega_{15}$ [ $\text{cm}^{-1}$ ]	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

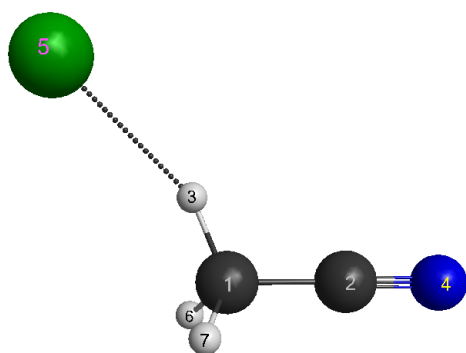


1	Y						
2	C	1	$r_1$				
3	H	2	$r_2$	1	$a_1$		
4	C	3	$r_3$	2	$a_2$	1	180.0
5	N	4	$r_4$	3	$a_3$	2	0.0
6	H	2	$r_5$	1	$a_4$	3	$d_1$
7	H	2	$r_5$	1	$a_4$	3	$-d_1$

Level <sup>a</sup>	MP2/aug-cc-pVDZ	CCSD(T)-F12b/aug-cc-pVDZ	CCSD(T)-F12b/aug-cc-pVTZ
<b>Energy [E<sub>h</sub>]</b>	-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
<b>ZPE [cm<sup>-1</sup>]</b>	9187	9207	9213
$\omega_1$ [cm <sup>-1</sup> ]	30i	37i	33i
$\omega_2$ [cm <sup>-1</sup> ]	28	26	28
$\omega_3$ [cm <sup>-1</sup> ]	39	29	35
$\omega_4$ [cm <sup>-1</sup> ]	163	149	150
$\omega_5$ [cm <sup>-1</sup> ]	187	150	150
$\omega_6$ [cm <sup>-1</sup> ]	529	522	520
$\omega_7$ [cm <sup>-1</sup> ]	901	885	888
$\omega_8$ [cm <sup>-1</sup> ]	916	910	909
$\omega_9$ [cm <sup>-1</sup> ]	1291	1290	1293
$\omega_{10}$ [cm <sup>-1</sup> ]	1444	1461	1465
$\omega_{11}$ [cm <sup>-1</sup> ]	1471	1485	1490
$\omega_{12}$ [cm <sup>-1</sup> ]	1949	2079	2075
$\omega_{13}$ [cm <sup>-1</sup> ]	3039	3052	3048
$\omega_{14}$ [cm <sup>-1</sup> ]	3189	3175	3173
$\omega_{15}$ [cm <sup>-1</sup> ]	3229	3201	3203

<sup>a</sup> 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

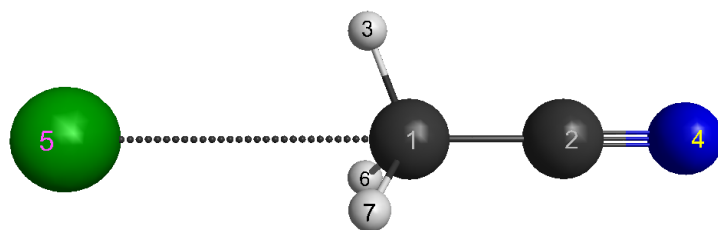


1	C						
2	C	1	$r_1$				
3	H	1	$r_2$	2	$a_1$		
4	N	2	$r_3$	1	$a_2$	3	0.0
5	Y	3	$r_4$	1	$a_3$	2	180.0
6	H	1	$r_5$	2	$a_4$	3	$d_1$
7	H	1	$r_5$	2	$a_4$	3	$-d_1$

Level <sup>a</sup>	MP2/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVTZ		
	F <sup>-</sup> ...CH <sub>3</sub> CN	Cl <sup>-</sup> ...CH <sub>3</sub> CN	Br <sup>-</sup> ...CH <sub>3</sub> CN	I <sup>-</sup> ...CH <sub>3</sub> CN	F <sup>-</sup> ...CH <sub>3</sub> CN	Cl <sup>-</sup> ...CH <sub>3</sub> CN	Br <sup>-</sup> ...CH <sub>3</sub> CN	F <sup>-</sup> ...CH <sub>3</sub> CN	Cl <sup>-</sup> ...CH <sub>3</sub> CN	Br <sup>-</sup> ...CH <sub>3</sub> CN
Energy [E <sub>h</sub> ]	-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 <sup>-1</sup> ]	9680	9926	9911	9874	9725	9979	9956	9738	9985	9966
$\omega_1$ [cm <sup>-1</sup> ]	98	50	39	2	98	47	22	98	47	34
$\omega_2$ [cm <sup>-1</sup> ]	296	149	118	88	293	145	110	293	147	109
$\omega_3$ [cm <sup>-1</sup> ]	309	176	153	106	310	166	132	309	155	122
$\omega_4$ [cm <sup>-1</sup> ]	403	375	373	366	413	384	379	412	383	381
$\omega_5$ [cm <sup>-1</sup> ]	431	380	375	370	443	389	382	443	389	382
$\omega_6$ [cm <sup>-1</sup> ]	936	927	927	925	927	919	918	928	919	918
$\omega_7$ [cm <sup>-1</sup> ]	1004	1016	1015	1009	1017	1026	1023	1021	1030	1028
$\omega_8$ [cm <sup>-1</sup> ]	1084	1055	1051	1044	1096	1067	1060	1100	1068	1063
$\omega_9$ [cm <sup>-1</sup> ]	1419	1390	1385	1372	1441	1409	1402	1446	1413	1406
$\omega_{10}$ [cm <sup>-1</sup> ]	1451	1448	1447	1446	1469	1464	1466	1472	1468	1468
$\omega_{11}$ [cm <sup>-1</sup> ]	1487	1464	1459	1453	1504	1483	1476	1511	1486	1481
$\omega_{12}$ [cm <sup>-1</sup> ]	2057	2165	2166	2167	2018	2288	2290	2016	2283	2286
$\omega_{13}$ [cm <sup>-1</sup> ]	2158	2957	3002	3060	2268	2943	3004	2264	2943	3001
$\omega_{14}$ [cm <sup>-1</sup> ]	3083	3124	3132	3154	3051	3092	3106	3055	3096	3106
$\omega_{15}$ [cm <sup>-1</sup> ]	3145	3176	3179	3187	3103	3137	3144	3107	3141	3146

<sup>a</sup> 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)<sup>a</sup> 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 <sup>b</sup>	MP2/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVTZ		
	Cl <sup>-</sup> ...CH <sub>3</sub> CN	Br <sup>-</sup> ...CH <sub>3</sub> CN	I <sup>-</sup> ...CH <sub>3</sub> CN	Cl <sup>-</sup> ...CH <sub>3</sub> CN	Br <sup>-</sup> ...CH <sub>3</sub> CN	I <sup>-</sup> ...CH <sub>3</sub> CN	Cl <sup>-</sup> ...CH <sub>3</sub> CN	Br <sup>-</sup> ...CH <sub>3</sub> CN	I <sup>-</sup> ...CH <sub>3</sub> CN
Energy [E <sub>h</sub> ]	-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 <sup>-1</sup> ]	9876	9872	9871	9874	9911	9931	9941	9938	9940
$\omega_1$ [cm <sup>-1</sup> ]	38	39	39	29i	26	37	30	34	35
$\omega_2$ [cm <sup>-1</sup> ]	38	39	39	29i	27	37	34	36	36
$\omega_3$ [cm <sup>-1</sup> ]	120	93	79	119	97	79	119	92	77
$\omega_4$ [cm <sup>-1</sup> ]	371	370	369	361	370	376	378	378	377
$\omega_5$ [cm <sup>-1</sup> ]	371	370	369	361	370	376	379	378	377
$\omega_6$ [cm <sup>-1</sup> ]	913	314	916	904	906	907	905	907	908
$\omega_7$ [cm <sup>-1</sup> ]	1005	1009	1014	1011	1021	1028	1021	1025	1031
$\omega_8$ [cm <sup>-1</sup> ]	1005	1010	1014	1011	1021	1028	1021	1026	1032
$\omega_9$ [cm <sup>-1</sup> ]	1335	1341	1348	1359	1367	1374	1364	1372	1381
$\omega_{10}$ [cm <sup>-1</sup> ]	1432	1435	1439	1453	1455	1459	1458	1461	1465
$\omega_{11}$ [cm <sup>-1</sup> ]	1432	1435	1439	1453	1455	1460	1458	1461	1465
$\omega_{12}$ [cm <sup>-1</sup> ]	2162	2164	2166	2287	2289	2291	2282	2284	2287
$\omega_{13}$ [cm <sup>-1</sup> ]	3113	3110	3106	3090	3085	3082	3090	3086	3081
$\omega_{14}$ [cm <sup>-1</sup> ]	3208	3206	3202	3170	3166	3164	3171	3167	3164
$\omega_{15}$ [cm <sup>-1</sup> ]	3208	3207	3203	3170	3167	3164	3171	3168	3164

<sup>a</sup> 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.

<sup>b</sup> For Br and I effective core potentials and the corresponding aug-cc-pVDZ-PP and aug-cc-pVTZ-PP basis sets are employed.