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Supplementary Material

On the bonding in bis-pyridine iodonium cations

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Cartesian Coordinates of M06-2X/def2-TZVP gas phase geometries. Ångstrom.

Iodine

7I, $[pyr\text{-}I\text{-}pyr]^+$
singlet

53	-0.000002	0.000041	-0.000020
6	2.921908	-0.819735	-0.819717
6	2.921927	0.819782	0.819645
6	4.302600	-0.846251	-0.846077
1	2.321958	-1.456801	-1.456830
6	4.302620	0.846132	0.846139
1	2.321991	1.456952	1.456669
6	5.003649	-0.000110	0.000074
1	4.811241	-1.520533	-1.520248
1	4.811282	1.520365	1.520342
6	-2.921945	0.819851	-0.819559
6	-2.921885	-0.819863	0.819607
6	-4.302638	0.846235	-0.845983
1	-2.322023	1.457080	-1.456536
6	-4.302576	-0.846348	0.846032
1	-2.321921	-1.457025	1.456611
6	-5.003647	-0.000089	0.000016
1	-4.811319	1.520556	-1.520085
1	-4.811198	-1.520697	1.520150
7	2.257720	0.000062	-0.000065
7	-2.257717	0.000025	0.000031
1	-6.085641	-0.000135	0.000014
1	6.085643	-0.000184	0.000133

8I, $[I\text{-}pyr]^+$
singlet

53	1.518444	-0.000001	0.000002
6	-1.199156	1.174893	-0.000039
6	-1.199165	-1.174872	0.000015
6	-2.576164	1.198309	0.000020
1	-0.597231	2.072423	0.000005
6	-2.576229	-1.198284	-0.000012
1	-0.597326	-2.072463	0.000011
6	-3.276376	-0.000002	-0.000001
1	-3.082978	2.153054	0.000058
1	-3.082987	-2.153058	-0.000014
7	-0.542277	-0.000030	-0.000012
1	-4.358503	0.000061	0.000025

[I-pyr]
doublet

53	1.852713	-0.000001	-0.000001
6	-1.617969	1.144978	0.000006
6	-1.618322	-1.145196	0.000006
6	-3.003976	1.194564	0.000000
1	-1.021052	2.050288	0.000008
6	-3.004347	-1.194355	0.000000
1	-1.021687	-2.050692	0.000008
6	-3.707699	0.000213	-0.000008
1	-3.513532	2.148195	-0.000005
1	-3.514197	-2.147828	-0.000006
7	-0.945619	-0.000213	0.000008
1	-4.790112	0.000381	-0.000016

I_2-pyr-pyr-I_2
singlet

53	6.218019	0.016299	0.013318
53	-6.226918	0.049771	0.033195
53	8.893223	-0.219501	-0.221673
53	-8.888055	-0.255704	-0.248394
6	2.814296	-0.909892	0.027686
6	1.430389	-0.927494	0.052668
6	0.742618	0.261711	0.276775
6	1.492097	1.418548	0.469924
6	2.874454	1.338561	0.433305
7	3.522051	0.198869	0.215499
1	3.381392	-1.815491	-0.156647
1	0.899311	-1.852440	-0.128062
1	1.010962	2.367142	0.668009
1	3.489504	2.218389	0.586085
6	-0.736992	0.288035	0.299311
6	-1.448601	1.348680	-0.253553
6	-1.463282	-0.757163	0.862795
6	-2.833163	1.313094	-0.233429
1	-0.936762	2.177858	-0.723728
6	-2.846386	-0.703544	0.841018
1	-0.962717	-1.594710	1.330048
7	-3.518574	0.307533	0.300408
1	-3.417922	2.115374	-0.669360
1	-3.442939	-1.499986	1.271650
6	-2.849143	-1.074226	0.364046
6	-1.463617	-1.126633	0.379294
6	-0.740020	-0.000006	-0.000035
6	-1.463630	1.126631	-0.379309
6	-2.849156	1.074222	-0.364019
7	-3.542833	-0.000006	0.000013
1	-3.429441	-1.940477	0.663252
1	-0.957789	-2.026079	0.705493
1	-0.957816	2.026091	-0.705493
1	-3.429465	1.940472	-0.663207
6	0.740020	0.000004	-0.000034
6	1.463616	1.126632	0.379295
6	1.463631	-1.126632	-0.379309
6	2.849142	1.074226	0.364046
1	0.957788	2.026078	0.705493
6	2.849157	-1.074221	-0.364019
1	0.957818	-2.026091	-0.705494
7	3.542833	0.000007	0.000013
1	3.429439	1.940478	0.663251
1	3.429466	-1.940470	-0.663207

I_2-pyr
singlet

53	0.168118	-0.001287	-0.000076
53	2.880016	0.000761	0.000114
6	-5.215334	0.002395	0.000638
6	-4.510730	1.196358	0.000218
6	-4.513766	-1.193341	0.000344
6	-3.125765	1.146515	-0.000386
1	-5.019379	2.150306	0.000458
6	-3.128660	-1.147007	-0.000430
1	-5.024831	-2.145994	0.000639
7	-2.455288	-0.001095	-0.000748
1	-2.525771	2.049609	-0.000463
1	-2.531024	-2.051654	-0.000924
1	-6.297531	0.003770	0.001212

1,4-bipyridine
singlet

Bromine

7Br, $[pyr\text{-}Br\text{-}pyr]^+$
singlet

35	0.000000	-0.000174	-0.000015
6	-2.744758	0.821253	-0.821341
6	-2.744833	-0.821174	0.821381
6	-4.125741	0.847019	-0.847001
1	-2.137838	1.454922	-1.455089
6	-4.125818	-0.846812	0.847049
1	-2.137964	-1.454887	1.455133
6	-4.825466	0.000135	0.000026
1	-4.635627	1.520854	-1.520644
1	-4.635771	-1.520590	1.520697
6	2.744854	-0.821370	-0.821195
6	2.744737	0.821424	0.821162
6	4.125840	-0.846949	-0.846882
1	2.138006	-1.455185	-1.454865
6	4.125719	0.847175	0.846875
1	2.137795	1.455159	1.454823
6	4.825466	0.000159	0.000002
1	4.635806	-1.520594	-1.520653
1	4.635592	1.520880	1.520658
7	-2.089944	0.000004	0.000015
7	2.089944	-0.000013	-0.000023
1	5.907451	0.000224	0.000013
1	-5.907452	0.000192	0.000035

[Br-pyr]
doublet

35	2.115838	0.000000	-0.000002
6	-1.041551	1.150611	0.000010
6	-1.041594	-1.150638	0.000000
6	-2.427602	1.196342	-0.000004
1	-0.434716	2.048536	0.000014
6	-2.427640	-1.196319	0.000001
1	-0.434783	-2.048579	0.000017
6	-3.128724	0.000026	-0.000008
1	-2.939070	2.148839	-0.000006
1	-2.939149	-2.148794	0.000007
7	-0.384697	-0.000022	0.000006
1	-4.211047	0.000039	-0.000008

8Br, $[Br\text{-}pyr]^+$
singlet

35	1.757364	-0.000001	0.000007
6	-0.746666	1.180468	-0.000067
6	-0.746666	-1.180453	0.000016
6	-2.123106	1.199715	0.000034
1	-0.135011	2.071121	-0.000016
6	-2.123136	-1.199704	-0.000020
1	-0.135054	-2.071138	0.000003
6	-2.821614	-0.000004	0.000006
1	-2.630950	2.153894	0.000099
1	-2.630943	-2.153902	-0.000015
7	-0.100694	-0.000014	-0.000028
1	-3.903803	0.000028	0.000051

Chlorine

7Cl, $[pyr\text{-}Cl\text{-}pyr]^+$
singlet

17	-0.000001	-0.000145	-0.000117
6	-2.611365	-0.822886	0.821455
6	-2.611348	0.822605	-0.821740
6	-3.992641	-0.848080	0.847187
1	-1.999289	-1.454836	1.452089
6	-3.992624	0.848313	-0.846987
1	-1.999261	1.454276	-1.452643
6	-4.691267	0.000268	0.000244
1	-4.503691	-1.521686	1.520183
1	-4.503660	1.522104	-1.519808
6	2.611259	0.821784	0.822595
6	2.611454	-0.821763	-0.822545
6	3.992533	0.847375	0.848104
1	1.999105	1.452632	1.454255
6	3.992733	-0.847163	-0.847925
1	1.999441	-1.452698	-1.454255
6	4.691267	0.000156	0.000120
1	4.503496	1.520463	1.521684
1	4.503860	-1.520179	-1.521452
7	-1.963267	-0.000248	-0.000245
7	1.963268	-0.000037	-0.000007
1	5.773241	0.000231	0.000174
1	-5.773240	0.000506	0.000470

[Cl-pyr]
doublet

17	2.629982	0.000000	0.000014
6	-0.341377	-1.154475	-0.000013
6	-0.341434	1.154512	-0.000022
6	-1.727587	-1.197822	0.000003
1	0.273648	-2.046164	-0.000024
6	-1.727642	1.197789	0.000009
1	0.273552	2.046229	-0.000022
6	-2.426871	-0.000035	0.000018
1	-2.240393	-2.149511	0.000012
1	-2.240498	2.149451	0.000025
7	0.303228	0.000033	-0.000032
1	-3.509139	-0.000058	0.000039

8Cl, $[Cl\text{-}pyr]^+$
singlet

17	-2.172987	-0.000001	-0.000001
6	0.161861	1.183338	-0.000031
6	0.161861	-1.183334	0.000018
6	1.537627	1.200721	0.000015
1	-0.458904	2.067694	-0.000013
6	1.537637	-1.200717	-0.000017
1	-0.458888	-2.067701	0.000003
6	2.235033	0.000000	0.000000
1	2.046455	2.154379	0.000040
1	2.046457	-2.154379	-0.000028
7	-0.479385	-0.000005	0.000013
1	3.317243	0.000008	0.000007

Fluorine

7F, $[pyr\text{-}F\text{-}pyr]^+$
singlet

9	0.664919	0.000001	-0.000006
6	-2.751212	0.758983	-0.847504
6	-2.751210	-0.758986	0.847502
6	-4.136962	0.794803	-0.887920
1	-2.170960	1.370636	-1.530439
6	-4.136961	-0.794802	0.887924
1	-2.170957	-1.370640	1.530434
6	-4.844222	0.000001	0.000003
1	-4.644077	1.431264	-1.599914
1	-4.644073	-1.431263	1.599921
6	2.603404	-0.954993	-0.710294
6	2.603400	0.954993	0.710292
6	3.981102	-0.966926	-0.718766
1	1.950834	-1.647195	-1.224847
6	3.981098	0.966927	0.718771
1	1.950827	1.647196	1.224842
6	4.673401	0.000001	0.000004
1	4.494230	-1.731212	-1.284574
1	4.494223	1.731213	1.284582
7	-2.058649	-0.000002	-0.000003
7	2.000887	0.000000	-0.000002
1	5.755439	0.000001	0.000007
1	-5.926452	0.000002	0.000006

8F, $[F\text{-}pyr]^+$
singlet

9	-2.190803	-0.000002	-0.000006
6	-0.253718	1.191791	0.000023
6	-0.253717	-1.191786	-0.000012
6	1.123756	1.205230	-0.000015
1	-0.903594	2.056161	0.000023
6	1.123764	-1.205225	0.000016
1	-0.903577	-2.056169	-0.000007
6	1.815794	-0.000001	-0.000003
1	1.636347	2.156689	-0.000022
1	1.636342	-2.156692	0.000020
7	-0.854505	-0.000004	0.000000
1	2.897962	0.000008	-0.000018

[F-pyr]
doublet

9	-2.707084	-0.000008	0.000078
6	-0.145154	1.156887	-0.000107
6	-0.145064	-1.156933	-0.000006
6	1.241893	1.199146	0.000047
1	-0.767003	2.043531	-0.000046
6	1.241999	-1.199091	-0.000011
1	-0.766825	-2.043641	-0.000051
6	1.939788	0.000052	0.000034
1	1.755623	2.150348	0.000139
1	1.755785	-2.150262	0.000012
7	-0.776663	-0.000053	-0.000087
1	3.022041	0.000106	0.000104

Calculated Energies of Dissociation Reactions

Table S1. Dissociation energies of **7I**, $[pyr\text{-}I\text{-}pyr]^+$. Units of kJ/mol. [a]

$[pyr\text{-}I\text{-}pyr]^+$		Heterolytic			Homolytic			Δ(Homo-Hetero)		
Method [b]		Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN
M06-2X/TZVP	ΔE_e	158.6	108.8	103.1	368.8	300.2	293.0	210.1	191.4	189.9
	ΔH	151.4	101.6	95.9	354.6	286.2	279.0	203.4	184.6	183.1
	ΔG	105.6	55.7	50.0	294.8	226.3	219.1	189.3	170.6	169.1
HF / TZVP	ΔG		12.7	6.8		83.2	76.1		70.5	69.3
MP2 / TZVP	ΔG		68.8	63.1		385.7	379.0		316.8	315.9
SCS-MP2 / TZVP	ΔG		57.6	51.9		370.5	363.9		312.9	312.0
SOS-MP2 / TZVP	ΔG		52.0	46.2		362.9	356.3		310.9	310.0
MP2 / TZVPP	ΔG		69.0	63.3		387.3	380.6		318.3	317.4
SCS-MP2 / TZVPP	ΔG		57.7	52.0		372.1	365.5		314.4	313.5
SOS-MP2 / TZVPP	ΔG		52.0	46.3		364.5	357.9		312.5	311.6
MP3 / TZVP	ΔG		45.4	39.6		293.8	287.1		248.4	247.4
MP4(SDQ) / TZVP	ΔG		63.4	45.9		294.3	281.4		230.9	235.5
CCSD / TZVP	ΔG		48.7	42.9		244.7	237.6		196.0	194.7
CCSD(T)/TZVP	ΔG		57.8	52.1		263.1	256.0		205.3	203.9

[a] Basis set notation refers to def2-TZVP (TZVP) and def2-TZVPP (TZVPP). All energies calculated at M06-2X/def2-TZVP optimized gas-phase geometries. Thermodynamic corrections taken from gas phase M06-2X/def2-TZVP calculations (standard state of T = 298.15 K and p = 1 atm).

[b] *Ab initio* ΔG results are a sum of the *ab initio* electronic energy and the M06-2X/def2-TZVP thermodynamic correction; ΔE_e results can be obtained by adding the difference between ΔG and ΔE_e with M02-2X/def2-TZVP (hetero 53.1, homo 73.9 kJ/mol).

Table S2. Dissociation energies of **7Br**, $[pyr\text{-}Br\text{-}pyr]^+$. Units of kJ/mol. [a]

$[pyr\text{-}Br\text{-}pyr]^+$		Heterolytic			Homolytic			Δ(Homo-Hetero)		
Method [b]		Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN
M06-2X/TZVP	ΔE_e	132.7	79.7	73.7	359.4	284.6	276.4	226.6	369.2	202.7
	ΔH	125.9	72.8	66.8	345.3	270.6	262.4	219.5	353.6	195.6
	ΔG	80.8	27.7	21.7	288.3	213.5	205.3	207.5	345.7	183.6
HF / TZVP	ΔG		-26.4	-32.6		55.8	48.3		82.2	80.9
MP2 / TZVP	ΔG		45.8	39.8		369.2	363.2		323.4	323.4
SCS-MP2 / TZVP	ΔG		32.9	26.9		353.6	347.6		320.6	320.7
SOS-MP2 / TZVP	ΔG		26.5	20.4		345.7	339.8		319.3	319.4
MP2 / TZVPP	ΔG		6.3	0.4		331.9	325.9		325.5	325.5
SCS-MP2 / TZVPP	ΔG		-11.2	-17.2		311.8	305.8		323.0	323.0
SOS-MP2 / TZVPP	ΔG		-20.0	-26.0		301.7	295.8		321.7	321.8
MP3 / TZVP	ΔG		14.0	8.0		272.5	266.0		258.4	258.0
MP4(SDQ) / TZVP	ΔG		21.2	15.0		261.8	255.0		240.6	240.0
CCSD / TZVP	ΔG		18.4	12.5		216.3	208.7		197.8	196.3
CCSD(T)/TZVP	ΔG		31.5	25.5		235.5	227.9		204.0	202.3

[a] Basis set notation refers to def2-TZVP (TZVP) and def2-TZVPP (TZVPP). All energies calculated at M06-2X/def2-TZVP optimized gas-phase geometries. Thermodynamic corrections taken from gas phase M06-2X/def2-TZVP calculations (standard state of T = 298.15 K and p = 1 atm).

[b] *Ab initio* ΔG results are a sum of the *ab initio* electronic energy and the M06-2X/def2-TZVP thermodynamic correction; ΔE_e results can be obtained by adding the difference between ΔG and ΔE_e with M02-2X/def2-TZVP (hetero 51.9, homo 71.1 kJ/mol).

Table S3. Dissociation energies of **7Cl**, [pyr-Cl-pyr]$^+$. Units of kJ/mol. [a]

[pyr-Cl-pyr]$^+$		Heterolytic			Homolytic			Δ(Homo-Hetero)		
Method [b]		Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN
M06-2X/TZVP	ΔE_e	96.7	41.5	35.3	346.7	266.9	257.9	250.0	225.4	222.6
	ΔH	90.4	35.1	29.0	332.4	252.6	243.6	242.0	217.5	214.6
	ΔG	46.4	-8.8	-15.0	276.3	196.5	187.5	229.9	205.3	202.5
HF / TZVP	ΔG		-77.1	-83.5		17.1	9.0		94.1	92.4
MP2 / TZVP	ΔG		14.6	8.4		422.7	413.5		408.0	405.1
SCS-MP2 / TZVP	ΔG		0.2	-6.0		405.7	396.9		405.5	402.9
SOS-MP2 / TZVP	ΔG		-7.0	-13.2		397.2	388.6		404.2	401.8
MP3 / TZVP	ΔG		-26.4	-32.6		292.6	283.8		319.0	316.4
MP4(SDQ) / TZVP	ΔG		-17.1	-23.5		268.5	260.0		285.6	283.4
CCSD / TZVP	ΔG		-20.5	-26.7		196.6	188.6		217.1	214.9
CCSD(T)/TZVP	ΔG		-3.7	-9.9		218.7	210.2		222.5	220.1

[a] Basis set notation refers to def2-TZVP (TZVP) and def2-TZVPP (TZVPP). All energies calculated at M06-2X/def2-TZVP optimized gas-phase geometries. Thermodynamic corrections taken from gas phase M06-2X/def2-TZVP calculations (standard state of T = 298.15 K and p = 1 atm).

[b] *Ab initio* ΔG results are a sum of the *ab initio* electronic energy and the M06-2X/def2-TZVP thermodynamic correction; ΔE_e results can be obtained by adding the difference between ΔG and ΔE_e with M02-2X/def2-TZVP (hetero 50.3, homo 70.4 kJ/mol).

Table S4. Dissociation energies of **7F**, [pyr-F-pyr]$^+$. Units of kJ/mol. [a]

[pyr-F-pyr]$^+$		Heterolytic			Homolytic			Δ(Homo-Hetero)		
Method [b]		Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN
M06-2X/TZVP	ΔE_e	26.8	1.8	-0.8	300.7	251.3	245.5	273.9	249.6	246.3
	ΔH	21.7	-3.3	-5.9	285.7	236.3	230.5	264.0	239.7	236.4
	ΔG	-6.6	-31.6	-34.1	243.4	194.0	188.2	250.0	225.7	222.3
HF / TZVP	ΔG		-38.9	-41.4		76.1	73.0		115.0	114.4
MP2 / TZVP	ΔG		-28.2	-30.8		418.4	411.8		446.5	442.6
SCS-MP2 / TZVP	ΔG		-30.2	-32.8		414.0	408.1		444.2	440.8
SOS-MP2 / TZVP	ΔG		-31.2	-33.8		411.8	406.2		443.0	440.0
MP3 / TZVP	ΔG		-30.6	-33.1		326.1	320.6		356.7	353.7
MP4(SDQ) / TZVP	ΔG		-30.1	-32.8		287.0	281.4		317.1	314.3
CCSD / TZVP	ΔG		-30.4	-33.0		207.2	202.2		237.7	235.2
CCSD(T)/TZVP	ΔG		-28.7	-31.3		212.6	207.4		241.4	238.7

[a] Basis set notation refers to def2-TZVP (TZVP) and def2-TZVPP (TZVPP). All energies calculated at M06-2X/def2-TZVP optimized gas-phase geometries. Thermodynamic corrections taken from gas phase M06-2X/def2-TZVP calculations (standard state of T = 298.15 K and p = 1 atm).

[b] *Ab initio* ΔG results are a sum of the *ab initio* electronic energy and the M06-2X/def2-TZVP thermodynamic correction; ΔE_e results can be obtained by adding the difference between ΔG and ΔE_e with M02-2X/def2-TZVP (hetero 33.4, homo 57.3 kJ/mol).

Table S5. Dissociation energies of **8I**, $[I\text{-}pyr]^+$. Units of kJ/mol. [a]

$[I\text{-}pyr]^+$		Heterolytic			Homolytic			Δ(Homo-Hetero)		
Method [b]		Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN
M06-2X/TZVP	ΔE_e	346.1	260.4	251.5	244.0	224.7	222.8	-102.0	-35.8	-28.7
	ΔH	341.7	256.1	247.1	235.4	216.0	214.2	-106.4	-40.1	-33.0
	ΔG	304.0	218.4	209.4	196.2	176.9	175.0	-107.8	-41.5	-34.4
HF / TZVP	ΔG		150.3	141.3		43.5	41.6		-106.8	-99.7
MP2 / TZVP	ΔG		281.0	272.1		327.2	325.7		46.2	53.6
SCS-MP2 / TZVP	ΔG		271.4	262.5		315.5	314.0		44.1	51.5
SOS-MP2 / TZVP	ΔG		266.6	257.8		309.7	308.2		43.1	50.5
MP2 / TZVPP	ΔG		280.4	271.5		328.7	327.3		48.3	55.7
SCS-MP2 / TZVPP	ΔG		270.7	261.8		317.1	315.6		46.4	53.8
SOS-MP2 / TZVPP	ΔG		265.8	257.0		311.3	309.8		45.5	52.9
MP3 / TZVP	ΔG		242.9	234.0		246.0	244.5		3.1	10.5
MP4(SDQ) / TZVP	ΔG		257.1	248.3		220.5	237.3		-36.6	-11.0
CCSD / TZVP	ΔG		251.3	242.5		199.1	197.4		-52.2	-45.1
CCSD(T)/TZVP	ΔG		266.6	257.8		215.0	213.3		-51.6	-44.5
MP3 / TZVPP	ΔG		242.4	233.6		247.4	245.9		5.0	12.3
MP4(SDQ) / TZVPP	ΔG		256.8	248.0		240.2	238.6		-16.6	-9.4
CCSD / TZVPP	ΔG		251.0	242.2		200.6	198.9		-50.4	-43.3
CCSD(T)/TZVPP	ΔG		266.2	257.4		216.6	214.9		-49.6	-42.5

[a] Basis set notation refers to def2-TZVP (TZVP) and def2-TZVPP (TZVPP). All energies calculated at M06-2X/def2-TZVP optimized gas-phase geometries. Thermodynamic corrections taken from gas phase M06-2X/def2-TZVP calculations (standard state of T = 298.15 K and p = 1 atm).

[b] *Ab initio* ΔG results are a sum of the *ab initio* electronic energy and the M06-2X/def2-TZVP thermodynamic correction; ΔE_e results can be obtained by adding the difference between ΔG and ΔE_e with M02-2X/def2-TZVP (hetero 42.1, homo 47.8 kJ/mol).

Table S6. Dissociation energies of **8Br**, $[Br\text{-}pyr]^+$. Units of kJ/mol. [a]

$[Br\text{-}pyr]^+$		Heterolytic			Homolytic			Δ(Homo-Hetero)		
Method [b]		Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN
M06-2X/TZVP	ΔE_e	509.1	410.1	400.0	269.0	254.3	253.0	-240.1	-155.8	-147.0
	ΔH	504.1	405.2	395.0	259.7	245.0	243.7	-244.4	-160.1	-151.3
	ΔG	465.2	366.2	356.1	219.4	204.7	203.4	-245.8	-161.5	-152.7
HF / TZVP	ΔG		254.1	243.9		48.3	46.8		-205.8	-197.0
MP2 / TZVP	ΔG		388.8	378.6		330.6	329.5		-58.2	-49.1
SCS-MP2 / TZVP	ΔG		380.0	369.8		318.0	317.0		-62.0	-52.9
SOS-MP2 / TZVP	ΔG		375.6	365.5		311.7	310.7		-63.9	-54.8
MP2 / TZVPP	ΔG		349.2	339.1		293.2	292.2		-56.0	-46.9
SCS-MP2 / TZVPP	ΔG		335.8	325.7		276.2	275.2		-59.6	-50.5
SOS-MP2 / TZVPP	ΔG		329.1	319.0		267.7	266.7		-61.4	-52.3
MP3 / TZVP	ΔG		360.7	350.6		254.5	240.5		-106.2	-97.2
MP4(SDQ) / TZVP	ΔG		365.4	355.1		241.6	202.4		-123.8	-114.7
CCSD / TZVP	ΔG		362.0	351.9		203.7	202.4		-158.3	-149.5
CCSD(T)/TZVP	ΔG		375.6	365.5		218.5	217.3		-157.1	-148.3

[a] Basis set notation refers to def2-TZVP (TZVP) and def2-TZVPP (TZVPP). All energies calculated at M06-2X/def2-TZVP optimized gas-phase geometries. Thermodynamic corrections taken from gas phase M06-2X/def2-TZVP calculations (standard state of T = 298.15 K and p = 1 atm).

[b] *Ab initio* ΔG results are a sum of the *ab initio* electronic energy and the M06-2X/def2-TZVP thermodynamic correction; ΔE_e results can be obtained by adding the difference between ΔG and ΔE_e with M02-2X/def2-TZVP (hetero 43.9, homo 49.6 kJ/mol).

Table S7. Dissociation energies of **8Cl**, $[Cl\text{-}pyr]^+$. Units of kJ/mol. [a]

$[Cl\text{-}pyr]^+$		Heterolytic			Homolytic			Δ(Homo-Hetero)		
Method [b]		Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN
M06-2X/TZVP	ΔE_e	671.6	560.0	548.6	306.9	295.8	294.7	-364.7	-264.2	-253.9
	ΔH	665.6	554.1	542.7	296.7	285.5	284.5	-369.0	-268.5	-258.2
	ΔG	626.4	514.8	503.4	256.0	244.9	243.8	-370.4	-269.9	-259.6
HF / TZVP	ΔG		71.3	374.4		358.5	70.1		-287.2	-304.3
MP2 / TZVP	ΔG		495.5	511.4		349.1	348.3		-146.4	-163.1
SCS-MP2 / TZVP	ΔG		488.4	504.3		336.7	335.9		-151.7	-168.4
SOS-MP2 / TZVP	ΔG		484.9	500.8		330.5	329.8		-154.4	-171.1
MP3 / TZVP	ΔG		472.7	488.6		276.8	276.0		-195.9	-212.6
MP4(SDQ) / TZVP	ΔG		470.9	486.7		259.8	259.0		-211.1	-227.7
CCSD / TZVP	ΔG		467.5	483.5		222.3	221.4		-245.1	-262.1
CCSD(T)/TZVP	ΔG		481.0	497.1		237.0	236.0		-244.1	-261.0

[a] Basis set notation refers to def2-TZVP (TZVP) and def2-TZVPP (TZVPP). All energies calculated at M06-2X/def2-TZVP optimized gas-phase geometries. Thermodynamic corrections taken from gas phase M06-2X/def2-TZVP calculations (standard state of T = 298.15 K and p = 1 atm).

[b] *Ab initio* ΔG results are a sum of the *ab initio* electronic energy and the M06-2X/def2-TZVP thermodynamic correction; ΔE_e results can be obtained by adding the difference between ΔG and ΔE_e with M02-2X/def2-TZVP (hetero 45.2, homo 50.9 kJ/mol).

Table S8. Dissociation energies of **8F**, $[F\text{-}pyr]^+$. Units of kJ/mol. [a]

$[F\text{-}pyr]^+$		Heterolytic			Homolytic			Δ(Homo-Hetero)		
Method [b]		Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN
M06-2X/TZVP	ΔE_e	1132.7	982.4	967.5	335.9	333.9	333.9	-796.9	-648.5	-633.6
	ΔH	1124.7	974.4	959.4	323.6	321.6	321.5	-801.2	-652.8	-637.9
	ΔG	1084.4	934.0	919.1	281.8	279.8	279.8	-802.6	-654.2	-639.3
HF / TZVP	ΔG		673.6	658.7		59.7	59.6		-613.9	-599.1
MP2 / TZVP	ΔG		912.7	897.7		380.3	380.5		-532.4	-517.2
SCS-MP2 / TZVP	ΔG		902.0	887.1		365.4	365.7		-536.6	-521.4
SOS-MP2 / TZVP	ΔG		896.7	881.8		358.0	358.2		-538.7	-523.5
MP3 / TZVP	ΔG		876.7	861.8		304.3	304.5		-572.4	-557.3
MP4(SDQ) / TZVP	ΔG		882.0	867.0		291.6	291.7		-590.5	-575.3
CCSD / TZVP	ΔG		878.2	863.3		253.1	253.1		-625.1	-610.2
CCSD(T)/TZVP	ΔG		892.2	877.3		267.7	267.7		-624.5	-609.7

[a] Basis set notation refers to def2-TZVP (TZVP) and def2-TZVPP (TZVPP). All energies calculated at M06-2X/def2-TZVP optimized gas-phase geometries. Thermodynamic corrections were taken from gas phase calculations (standard state of T = 298.15 K and p = 1 atm).

[b] *Ab initio* ΔG results are a sum of the *ab initio* electronic energy and the M06-2X/def2-TZVP thermodynamic correction; ΔE_e results can be obtained by adding the difference between ΔG and ΔE_e with M02-2X/def2-TZVP (hetero 48.3, homo 54.0 kJ/mol).

Table S9. Dissociation energies of $[I\text{-}PMe_3]^+$. Units of kJ/mol. [a]

$[I\text{-}PMe_3]^+$		Heterolytic			Homolytic			Δ(Homo-Hetero)		
Method [b]		Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN
M06-2X/TZVP	ΔE_e	512.0	427.9	420.8	270.6	245.1	243.5	-241.4	-182.9	-177.3
	ΔH	508.1	418.0	416.9	267.0	235.1	239.9	-241.1	-183.0	-177.0
	ΔG	470.5	376.5	379.3	226.4	190.9	199.3	-244.0	-185.6	-179.9
HF / TZVP	ΔG		388.9	382.2		161.3	160.0		-227.6	-222.2
MP2 / TZVP	ΔG		469.4	462.5		267.9	266.4		-201.5	-196.0
SCS-MP2 / TZVP	ΔG		448.4	441.5		252.2	250.7		-196.2	-190.7
SOS-MP2 / TZVP	ΔG		437.8	431.0		244.4	242.9		-193.5	-188.1
MP2 / TZVPP	ΔG		467.4	460.5		269.9	268.4		-197.5	-192.0
SCS-MP2 / TZVPP	ΔG		446.0	439.1		254.1	252.6		-191.9	-186.5
SOS-MP2 / TZVPP	ΔG		435.3	428.5		246.2	244.7		-189.1	-183.7
MP3 / TZVP	ΔG		414.6	417.6		219.4	228.0		-195.2	-189.6
MP4(SDQ) / TZVP	ΔG		420.3	423.3		222.2	230.8		-198.1	-192.5
CCSD / TZVP	ΔG		415.7	418.7		217.4	226.0		-198.2	-192.7
CCSD(T)/TZVP	ΔG		427.9	430.9		232.1	240.7		-195.9	-190.3

[a] Basis set notation refers to def2-TZVP (TZVP) and def2-TZVPP (TZVPP). All energies calculated at M06-2X/def2-TZVP optimized gas-phase geometries. Thermodynamic corrections taken from gas phase M06-2X/def2-TZVP calculations (standard state of T = 298.15 K and p = 1 atm).

[b] *Ab initio* ΔG results are a sum of the *ab initio* electronic energy and the M06-2X/def2-TZVP thermodynamic correction; ΔE_e results can be obtained by adding the difference between ΔG and ΔE_e with M02-2X/def2-TZVP (hetero 41.6, homo 44.2 kJ/mol).

Table S10. Dissociation energies of $[Br\text{-}PMe_3]^+$. Units of kJ/mol. [a]

$[Br\text{-}PMe_3]^+$		Heterolytic			Homolytic			Δ(Homo-Hetero)		
Method [b]		Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN
M06-2X/TZVP	ΔE_e	717.7	630.3	622.2	338.3	327.4	326.5	-379.5	-302.9	-295.6
	ΔH	713.0	618.2	617.4	333.8	315.1	322.0	-379.2	-303.0	-295.3
	ΔG	673.9	568.1	578.3	291.8	268.7	280.1	-382.1	-299.4	-298.3
HF / TZVP	ΔG		482.2	492.6		159.1	170.5		-323.2	-322.2
MP2 / TZVP	ΔG		620.5	612.4		314.6	313.6		-305.9	-298.7
SCS-MP2 / TZVP	ΔG		601.7	593.6		299.5	298.5		-302.2	-295.1
SOS-MP2 / TZVP	ΔG		592.3	584.3		291.9	291.0		-300.4	-293.3
MP2 / TZVPP	ΔG		617.7	609.6		315.9	314.9		-301.9	-294.7
SCS-MP2 / TZVPP	ΔG		598.7	590.6		300.7	299.7		-298.0	-290.9
SOS-MP2 / TZVPP	ΔG		589.2	581.1		293.1	292.1		-296.0	-289.0
MP3 / TZVP	ΔG		570.6	580.9		266.1	283.7		+304.5	-297.2
MP4(SDQ) / TZVP	ΔG		565.8	576.1		262.3	279.8		-303.4	-296.2
CCSD / TZVP	ΔG		563.6	573.9		259.3	276.8		-304.3	-297.1
CCSD(T)/TZVP	ΔG		573.1	583.3		271.7	289.2		-301.4	-294.1

[a] Basis set notation refers to def2-TZVP (TZVP) and def2-TZVPP (TZVPP). All energies calculated at M06-2X/def2-TZVP optimized gas-phase geometries. Thermodynamic corrections were taken from gas phase calculations (standard state of T = 298.15 K and p = 1 atm).

[b] *Ab initio* ΔG results are a sum of the *ab initio* electronic energy and the M06-2X/def2-TZVP thermodynamic correction; ΔE_e results can be obtained by adding the difference between ΔG and ΔE_e with M02-2X/def2-TZVP (hetero 43.8, homo 46.4 kJ/mol).

Table S11. Dissociation energies of $[Cl\text{-}PMe_3]^+$. Units of kJ/mol. [a]

$[Cl\text{-}PMe_3]^+$		Heterolytic			Homolytic			Δ(Homo-Hetero)		
Method [b]		Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN
M06-2X/TZVP	ΔE_e	906.1	805.2	795.9	402.0	393.9	393.4	-504.0	-411.3	-402.5
	ΔH	901.3	792.8	791.1	397.5	381.4	388.9	-503.8	-411.4	-402.2
	ΔG	862.7	743.2	752.6	356.0	335.4	347.4	-506.7	-407.8	-405.1
HF / TZVP	ΔG		617.4	654.3		212.8	224.8		-404.6	-429.4
MP2 / TZVP	ΔG		760.8	778.8		366.7	366.1		-394.1	-412.7
SCS-MP2 / TZVP	ΔG		744.3	762.3		352.3	351.7		-392.0	-410.7
SOS-MP2 / TZVP	ΔG		746.0	754.1		345.1	344.5		-390.9	-409.6
MP2 / TZVPP	ΔG		759.0	749.6		368.4	367.8		-390.6	-381.9
SCS-MP2 / TZVPP	ΔG		742.4	733.1		353.9	353.3		-388.5	-379.8
SOS-MP2 / TZVPP	ΔG		734.1	724.9		346.7	346.1		-387.4	-378.8
MP3 / TZVP	ΔG		713.7	723.1		319.6	337.8		-394.2	-385.4
MP4(SDQ) / TZVP	ΔG		703.0	739.8		312.3	330.5		-390.7	-409.3
CCSD / TZVP	ΔG		700.5	704.2		309.3	290.9		-391.2	-413.2
CCSD(T)/TZVP	ΔG		709.9	716.6		321.6	313.5		-388.3	-403.1

[a] Basis set notation refers to def2-TZVP (TZVP) and def2-TZVPP (TZVPP). All energies calculated at M06-2X/def2-TZVP optimized gas-phase geometries. Thermodynamic corrections were taken from gas phase calculations (standard state of $T = 298.15$ K and $p = 1$ atm).

[b] *Ab initio* ΔG results are a sum of the *ab initio* electronic energy and the M06-2X/def2-TZVP thermodynamic correction; ΔE_e results can be obtained by adding the difference between ΔG and ΔE_e with M02-2X/def2-TZVP (hetero 43.4, homo 46.0 kJ/mol).

Table S12. Dissociation energies of $[F\text{-}PMe_3]^+$. Units of kJ/mol. [a]

$[F\text{-}PMe_3]^+$		Heterolytic			Homolytic			Δ(Homo-Hetero)		
Method [b]		Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN	Gas phase	CH_2Cl_2	CH_3CN
M06-2X/TZVP	ΔE_e	1501.0	1361.4	1348.4	564.7	565.8	566.2	-936.2	-795.6	-782.2
	ΔH	1493.1	1341.8	1340.6	557.2	546.1	558.6	-935.9	-795.7	-781.9
	ΔG	1453.0	1287.6	1300.5	514.2	495.5	515.6	-938.9	-792.1	-784.9
HF / TZVP	ΔG		1069.6	1082.6		338.3	358.4		-731.3	-724.2
MP2 / TZVP	ΔG		1322.0	1309.0		541.9	542.2		-780.1	-766.8
SCS-MP2 / TZVP	ΔG		1302.9	1290.0		526.0	526.3		-776.9	-763.7
SOS-MP2 / TZVP	ΔG		1293.3	1280.5		518.1	518.4		-775.3	-762.1
MP2 / TZVPP	ΔG		1318.5	1305.5		542.5	542.7		-776.1	-762.8
SCS-MP2 / TZVPP	ΔG		1299.2	1286.3		526.6	526.9		-772.6	-759.4
SOS-MP2 / TZVPP	ΔG		1289.6	1276.7		518.7	518.9		-770.9	-757.7
MP3 / TZVP	ΔG		1242.8	1255.8		472.2	498.4		-770.7	-757.3
MP4(SDQ) / TZVP	ΔG		1247.7	1260.6		477.6	503.8		-770.1	-756.8
CCSD / TZVP	ΔG		1243.6	1256.3		472.5	498.7		-771.2	-757.9
CCSD(T)/TZVP	ΔG		1251.2	1264.1		482.5	508.6		-768.8	-755.5

[a] Basis set notation refers to def2-TZVP (TZVP) and def2-TZVPP (TZVPP). All energies calculated at M06-2X/def2-TZVP optimized gas-phase geometries. Thermodynamic corrections were taken from gas phase calculations (standard state of T = 298.15 K and p = 1 atm).

[b] *Ab initio* ΔG results are a sum of the *ab initio* electronic energy and the M06-2X/def2-TZVP thermodynamic correction; ΔE_e results can be obtained by adding the difference between ΔG and ΔE_e with M02-2X/def2-TZVP (hetero 47.9, homo 50.6 kJ/mol).

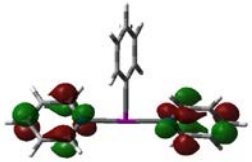
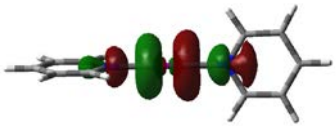
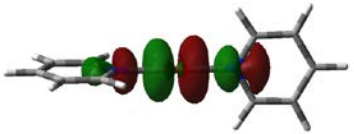
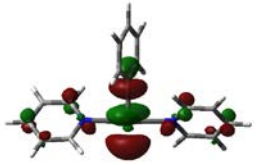
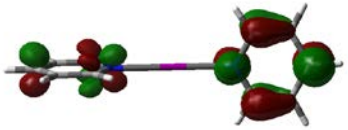
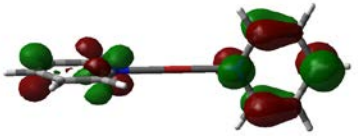
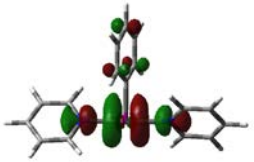
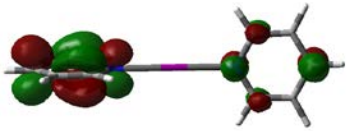
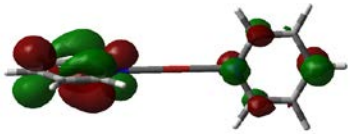
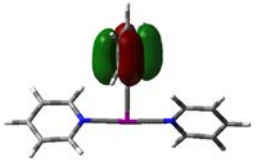
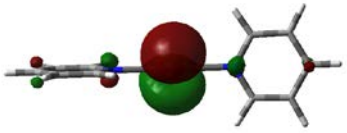
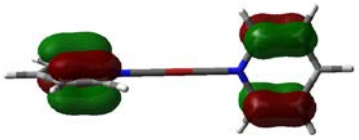
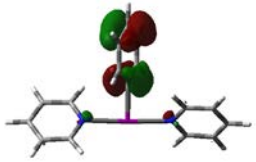
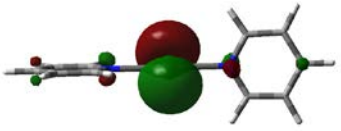
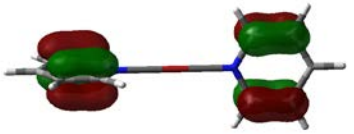
Molecular orbital	**10** $[PhI(pyr)_2]^{2+}$	**7I** $[pyr\text{-}I\text{-}pyr]^{+}$	**7Br** $[pyr\text{-}Br\text{-}pyr]^{+}$
LUMO+2			
LUMO+1			
LUMO			
HOMO			
HOMO-1			

Figure S1. Key molecular orbitals of halo-pyridinium cations **10** and **7X** (X = I, Br, Cl, F).

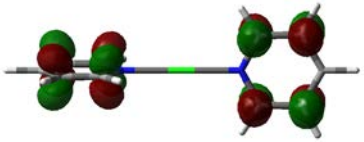
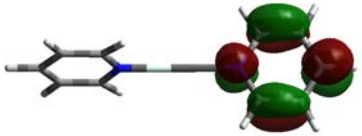
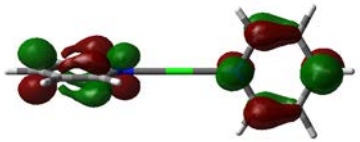
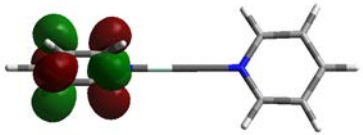
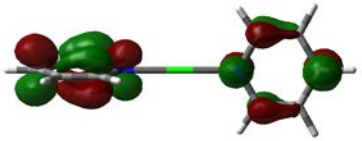
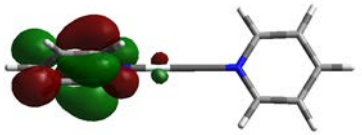
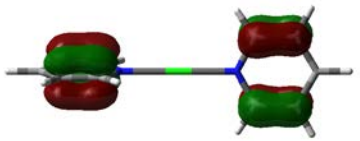
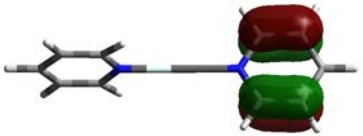
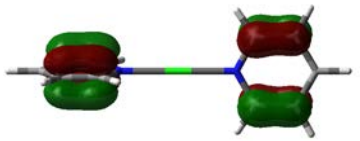
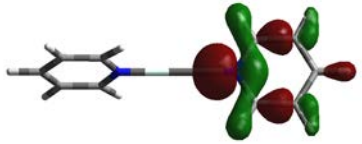
Molecular orbital	**7Cl** [pyr-Cl-pyr]$^+$	**7F** [pyr-F-pyr]$^+$
LUMO+2		
LUMO+1		
LUMO		
HOMO		
HOMO-1		

Figure S1 continued. Key molecular orbitals of halo-pyridinium cations **7X** (X = I, Br, Cl, F) and **10**.

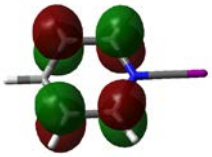
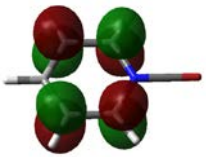
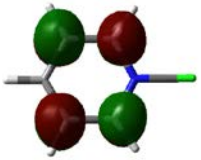
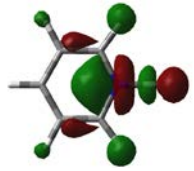
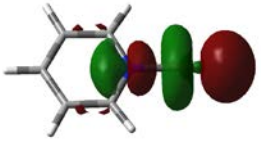
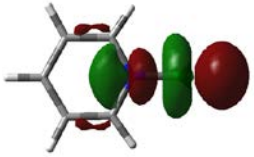
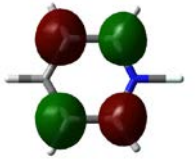
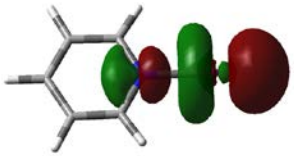
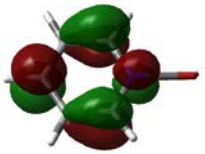
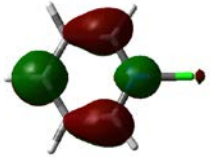
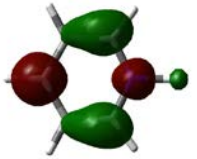
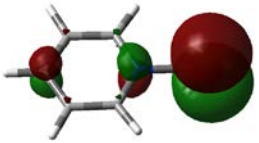
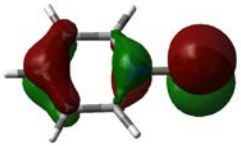
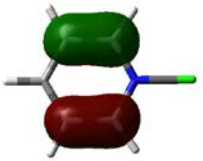
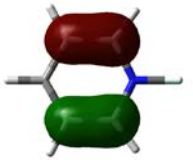
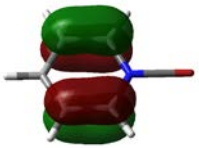
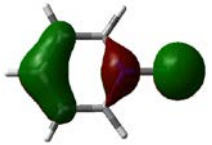
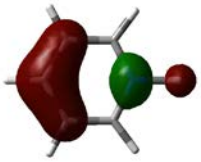
Molecular orbital	**8I** [pyr-I]$^+$	**8Br** [pyr-Br]$^+$	**8Cl** [pyr-Cl]$^+$	**8F** [pyr-F]$^+$
LUMO+2				
LUMO+1				
LUMO				
HOMO				
HOMO-1				

Figure S2. Important molecular orbitals of **8I** and **8Br**.