Photostability via sloped conical intersections: a computational study of the pyrene radical cation

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Supporting Information

Contents

MMVB optimized Cartesian coordinates in Å.

D_0 minimum

C	0.00000	-3.54628	0.00000
C	0.00000	3.54628	0.00000
C	1.21427	-2.85105	0.00000
C	-1.21427	-2.85105	0.00000
C	1.21427	2.85105	0.00000
C	-1.21427	2.85105	0.00000
C	1.23143	-1.42199	0.00000
C	-1.23143	-1.42199	0.00000
C	1.23143	1.42199	0.00000
C	-1.23143	1.42199	0.00000
C	2.45171	-0.69602	0.00000
C	-2.45171	-0.69602	0.00000
C	2.45171	0.69602	0.00000
C	-2.45171	0.69602	0.00000
C	0.00000	-0.71089	0.00000
C	0.00000	0.71089	0.00000
H	0.00000	-4.66117	0.00000
H	0.00000	4.66117	0.00000
H	2.17229	-3.42085	0.00000
H	-2.17229	-3.42085	0.00000
H	2.17229	3.42085	0.00000
H	-2.17229	3.42085	0.00000
H	3.42342	-1.24240	0.00000
H	-3.42342	-1.24240	0.00000
H	3.42342	1.24240	0.00000
H	-3.42342	1.24240	0.00000

D_1 minimum

C	0.00000	-3.49216	0.00000
C	0.00000	3.49216	0.00000
C	1.23627	-2.79337	0.00000
C	-1.23627	-2.79337	0.00000
C	1.23627	2.79337	0.00000
C	-1.23627	2.79337	0.00000
C	1.25757	-1.40794	0.00000
C	-1.25757	-1.40794	0.00000
C	1.25757	1.40794	0.00000
C	-1.25757	1.40794	0.00000
C	2.52184	-0.67884	0.00000
C	-2.52184	-0.67884	0.00000
C	2.52184	0.67884	0.00000
C	-2.52184	0.67884	0.00000
C	0.00000	-0.69067	0.00000
C	0.00000	0.69067	0.00000
H	0.00000	-4.60695	0.00000
H	0.00000	4.60695	0.00000
H	2.19072	-3.36903	0.00000
H	-2.19072	-3.36903	0.00000
H	2.19072	3.36903	0.00000
H	-2.19072	3.36903	0.00000
H	3.48941	-1.23282	0.00000
H	-3.48941	-1.23282	0.00000
H	3.48941	1.23282	0.00000
H	-3.48941	1.23282	0.00000

D_2 minimum

C	.00000	-3.56520	.000000
C	.00000	3.56520	.000000
C	1.21906	-2.87074	.000000
C	-1.21906	-2.87074	.000000
C	1.21906	2.87074	.000000
C	-1.21906	2.87074	.000000
C	1.23012	-1.45412	.000000
C	-1.23012	-1.45412	.000000
C	1.23012	1.45412	.000000
C	-1.23012	1.45412	.000000
C	2.44867	-.70475	.000000
C	-2.44867	-.70475	.000000
C	2.44867	.70475	.000000
C	-2.44867	.70475	.000000
C	.00000	-.74029	.000000
C	.00000	.74029	.000000
H	.00000	-4.67948	.000000
H	.00000	4.67948	.000000
H	2.17854	-3.43796	.000000
H	-2.17854	-3.43796	.000000
H	2.17854	3.43796	.000000
H	-2.17854	3.43796	.000000
H	3.42535	-1.24348	.000000
H	-3.42535	-1.24348	.000000
H	3.42535	1.24348	.000000
H	-3.42535	1.24348	.000000

D_0/D_1 conical intersection

C	0.00000	-3.48735	0.00000
C	0.00000	3.48735	0.00000
C	1.23844	-2.78823	0.00000
C	-1.23844	-2.78823	0.00000
C	1.23844	2.78823	0.00000
C	-1.23844	2.78823	0.00000
C	1.26008	-1.40677	0.00000
C	-1.26008	-1.40677	0.00000
C	1.26008	1.40677	0.00000
C	-1.26008	1.40677	0.00000
C	2.52864	-0.67719	0.00000
C	-2.52864	-0.67719	0.00000
C	2.52864	0.67719	0.00000
C	-2.52864	0.67719	0.00000
C	0.00000	-0.68877	0.00000
C	0.00000	0.68877	0.00000
H	0.00000	-4.60214	0.00000
H	0.00000	4.60214	0.00000
H	2.19243	-3.36473	0.00000
H	-2.19243	-3.36473	0.00000
H	2.19243	3.36473	0.00000
H	-2.19243	3.36473	0.00000
H	3.49588	-1.23173	0.00000
H	-3.49588	-1.23173	0.00000
H	3.49588	1.23173	0.00000
H	-3.49588	1.23173	0.00000

D_1/D_2 conical intersection

C	.00000	-3.64170	.000000
C	.00000	3.64170	.000000
C	1.20165	-2.94498	.000000
C	-1.20165	-2.94498	.000000
C	1.20165	2.94498	.000000
C	-1.20165	2.94498	.000000
C	1.20313	-1.49277	.000000
C	-1.20313	-1.49277	.000000
C	1.20313	1.49277	.000000
C	-1.20313	1.49277	.000000
C	2.37744	-.73145	.000000
C	-2.37744	-.73145	.000000
C	2.37744	.73145	.000000
C	-2.37744	.73145	.000000
C	.00000	-.77316	.000000
C	.00000	.77316	.000000
H	.00000	-4.75668	.000000
H	.00000	4.75668	.000000
H	2.16565	-3.50462	.000000
H	-2.16565	-3.50462	.000000
H	2.16565	3.50462	.000000
H	-2.16565	3.50462	.000000
H	3.35936	-1.25865	.000000
H	-3.35936	-1.25865	.000000
H	3.35936	1.25865	.000000
H	-3.35936	1.25865	.000000

CASSCF(15,16)/6-31G* optimized Cartesian coordinates in Å.

$D_0(B_{2g})$ D_{2h} minimum

C	0.0000000000	-3.5352442705	0.0000000000
C	0.0000000000	3.5352442705	0.0000000000
C	1.2058019708	-2.8395285394	0.0000000000
C	-1.2058019708	-2.8395285394	0.0000000000
C	1.2058019708	2.8395285394	0.0000000000
C	-1.2058019708	2.8395285394	0.0000000000
C	1.2292702766	-1.4177749540	0.0000000000
C	-1.2292702766	-1.4177749540	0.0000000000
C	1.2292702766	1.4177749540	0.0000000000
C	-1.2292702766	1.4177749540	0.0000000000
C	2.4442105071	-0.6915928655	0.0000000000
C	-2.4442105071	-0.6915928655	0.0000000000
C	2.4442105071	0.6915928655	0.0000000000
C	-2.4442105071	0.6915928655	0.0000000000
C	0.0000000000	-0.7082318373	0.0000000000
C	0.0000000000	0.7082318373	0.0000000000
H	0.0000000000	-4.6083695599	0.0000000000
H	0.0000000000	4.6083695599	0.0000000000
H	2.1359953431	-3.3770009029	0.0000000000
H	-2.1359953431	-3.3770009029	0.0000000000
H	2.1359953431	3.3770009029	0.0000000000
H	-2.1359953431	3.3770009029	0.0000000000
H	3.3764600827	-1.2253344450	0.0000000000
H	-3.3764600827	-1.2253344450	0.0000000000
H	3.3764600827	1.2253344450	0.0000000000
H	-3.3764600827	1.2253344450	0.0000000000

$D_1(B_{3g})$ D_{2h} minimum

C	0.0000000000	-3.4937413641	0.0000000000
C	0.0000000000	3.4937413641	0.0000000000
C	1.2264633276	-2.8054782551	0.0000000000
C	-1.2264633276	-2.8054782551	0.0000000000
C	1.2264633276	2.8054782551	0.0000000000
C	-1.2264633276	2.8054782551	0.0000000000
C	1.2517050565	-1.4207034128	0.0000000000
C	-1.2517050565	-1.4207034128	0.0000000000
C	1.2517050565	1.4207034128	0.0000000000
C	-1.2517050565	1.4207034128	0.0000000000
C	2.4955696502	-0.6764403665	0.0000000000
C	-2.4955696502	-0.6764403665	0.0000000000
C	2.4955696502	0.6764403665	0.0000000000
C	-2.4955696502	0.6764403665	0.0000000000
C	0.0000000000	-0.6975934461	0.0000000000
C	0.0000000000	0.6975934461	0.0000000000
H	0.0000000000	-4.5675501602	0.0000000000
H	0.0000000000	4.5675501602	0.0000000000
H	2.1460237456	-3.3598618916	0.0000000000
H	-2.1460237456	-3.3598618916	0.0000000000
H	2.1460237456	3.3598618916	0.0000000000
H	-2.1460237456	3.3598618916	0.0000000000
H	3.4175355413	-1.2267961620	0.0000000000
H	-3.4175355413	-1.2267961620	0.0000000000
H	3.4175355413	1.2267961620	0.0000000000
H	-3.4175355413	1.2267961620	0.0000000000

$D_2(B_{1u})$ D_{2h} minimum

C	0.0000000000	-3.5443345986	0.0000000000
C	0.0000000000	3.5443345986	0.0000000000
C	1.2115945520	-2.8559288321	0.0000000000
C	-1.2115945520	-2.8559288321	0.0000000000
C	1.2115945520	2.8559288321	0.0000000000
C	-1.2115945520	2.8559288321	0.0000000000
C	1.2356851207	-1.4516160587	0.0000000000
C	-1.2356851207	-1.4516160587	0.0000000000
C	1.2356851207	1.4516160587	0.0000000000
C	-1.2356851207	1.4516160587	0.0000000000
C	2.4410545005	-0.6956286617	0.0000000000
C	-2.4410545005	-0.6956286617	0.0000000000
C	2.4410545005	0.6956286617	0.0000000000
C	-2.4410545005	0.6956286617	0.0000000000
C	0.0000000000	-0.7369398422	0.0000000000
C	0.0000000000	0.7369398422	0.0000000000
H	0.0000000000	-4.6177863792	0.0000000000
H	0.0000000000	4.6177863792	0.0000000000
H	2.1394901726	-3.3968641755	0.0000000000
H	-2.1394901726	-3.3968641755	0.0000000000
H	2.1394901726	3.3968641755	0.0000000000
H	-2.1394901726	3.3968641755	0.0000000000
H	3.3795004496	-1.2180338136	0.0000000000
H	-3.3795004496	-1.2180338136	0.0000000000
H	3.3795004496	1.2180338136	0.0000000000
H	-3.3795004496	1.2180338136	0.0000000000

CASSCF(13,14)/6-31G* optimized Cartesian coordinates in Å.

D_0/D_1 D_{2h} conical intersection

C	0.0000000000	-3.4703945066	0.0000000000
C	0.0000000000	3.4703945066	0.0000000000
C	1.2354153673	-2.7858362879	0.0000000000
C	-1.2354153673	-2.7858362879	0.0000000000
C	1.2354153673	2.7858362879	0.0000000000
C	-1.2354153673	2.7858362879	0.0000000000
C	1.2609064316	-1.4172995212	0.0000000000
C	-1.2609064316	-1.4172995212	0.0000000000
C	1.2609064316	1.4172995212	0.0000000000
C	-1.2609064316	1.4172995212	0.0000000000
C	2.5214141780	-0.6694058628	0.0000000000
C	-2.5214141780	-0.6694058628	0.0000000000
C	2.5214141780	0.6694058628	0.0000000000
C	-2.5214141780	0.6694058628	0.0000000000
C	0.0000000000	-0.6859104025	0.0000000000
C	0.0000000000	0.6859104025	0.0000000000
H	0.0000000000	-4.5446190675	0.0000000000
H	0.0000000000	4.5446190675	0.0000000000
H	2.1502492108	-3.3474792850	0.0000000000
H	-2.1502492108	-3.3474792850	0.0000000000
H	2.1502492108	3.3474792850	0.0000000000
H	-2.1502492108	3.3474792850	0.0000000000
H	3.4368636272	-1.2300692382	0.0000000000
H	-3.4368636272	-1.2300692382	0.0000000000
H	3.4368636272	1.2300692382	0.0000000000
H	-3.4368636272	1.2300692382	0.0000000000

D_1/D_2 D_{2h} conical intersection

C	0.0000000000	-3.5942028808	0.0000000000
C	0.0000000000	3.5942028808	0.0000000000
C	1.1929851919	-2.9049671261	0.0000000000
C	-1.1929851919	-2.9049671261	0.0000000000
C	1.1929851919	2.9049671261	0.0000000000
C	-1.1929851919	2.9049671261	0.0000000000
C	1.2111223296	-1.4784949338	0.0000000000
C	-1.2111223296	-1.4784949338	0.0000000000
C	1.2111223296	1.4784949338	0.0000000000
C	-1.2111223296	1.4784949338	0.0000000000
C	2.3779662335	-0.7163048153	0.0000000000
C	-2.3779662335	-0.7163048153	0.0000000000
C	2.3779662335	0.7163048153	0.0000000000
C	-2.3779662335	0.7163048153	0.0000000000
C	0.0000000000	-0.7709185869	0.0000000000
C	0.0000000000	0.7709185869	0.0000000000
H	0.0000000000	-4.6673267819	0.0000000000
H	0.0000000000	4.6673267819	0.0000000000
H	2.1313164268	-3.4284508161	0.0000000000
H	-2.1313164268	-3.4284508161	0.0000000000
H	2.1313164268	3.4284508161	0.0000000000
H	-2.1313164268	3.4284508161	0.0000000000
H	3.3326971720	-1.2095575312	0.0000000000
H	-3.3326971720	-1.2095575312	0.0000000000
H	3.3326971720	1.2095575312	0.0000000000
H	-3.3326971720	1.2095575312	0.0000000000

Table S1. MMVB energies (a.u.) of states D_0, D_1, and D_2 at the PES minima and at the D_0/D_1 and D_1/D_2 conical intersections.

Geometry/State	D_0	D_1	D_2
D_0 minimum	-1.045809	-1.011632	-0.970883
D_1 minimum	-1.030080	-1.027086	-0.958685
D_2 minimum	-1.041979	-1.007845	-0.974928
D_0/D_1 CI	-1.026937	-1.026923	-0.957178
D_1/D_2 CI	-1.023130	-0.962611	-0.962385

Table S2. Distribution of the positive charge over atoms of pyrene radical cation for different electronic states at critical spatial configurations.

Geometry	State	Atom 1	Atom 2	Atom 3a	Atom 3a[1]	Atom 4
	D_0	0.0576	0.0304	0.0749	0.0693	0.0677
D_0 minimum	D_1	0.0529	0.0628	0.0741	0.1120	0.0357
	D_2	0.0292	0.0223	0.0598	0.0943	0.1027
	D_0	0.0568	0.0305	0.0740	0.0693	0.0694
D_1 minimum	D_1	0.0518	0.0616	0.0745	0.1184	0.0337
	D_2	0.0501	0.0579	0.0624	0.0296	0.0938
	D_0	0.0577	0.0304	0.0743	0.0673	0.0692
D_2 minimum	D_1	0.0541	0.0659	0.0730	0.1112	0.0343
	D_2	0.0311	0.0254	0.0593	0.0885	0.1027
	D_0	0.0567	0.0306	0.0738	0.0692	0.0695
D_0/D_1 CI	D_1	0.0517	0.0616	0.0745	0.1188	0.0336
	D_2	0.0518	0.0606	0.0643	0.0368	0.0852
	D_0	0.0601	0.0315	0.0740	0.0651	0.0676
D_1/D_2 CI	D_1	0.0568	0.0705	0.0714	0.0999	0.0366
	D_2	0.0276	0.0191	0.0629	0.1039	0.0980

The geometry of the critical points on the PESs provides one way to characterize the states. Alternatively, their electronic structure can be partly understood on the basis of the charge distribution in the cation. Although the charges determined in the framework of the MMVB method are not quite reliable, because they are obtained from the wavefunction with ionic states projected out, their values and changes still can characterize the states. One can see that the charge distributions for the three states are quite distinctive.

Table S3. CASSCF(15,16)/6-31G* energies (a.u.) of states D_0, D_1, and D_2 at the PES minima and at the D_0/D_1 and D_1/D_2 conical intersections.

Geometry/State	B_{2g} energy	B_{3g} energy	B_{1u} energy
D_0 minimum	-611.729381	-611.692947	-611.665736
D_1 minimum	-611.716902	-611.705185	-611.657744
D_2 minimum	-611.724624	-611.692250	-611.670342
D_0/D_1 CI[a]	-611.702012	-611.702202	
D_1/D_2 CI[a]		-611.653558	-611.657473

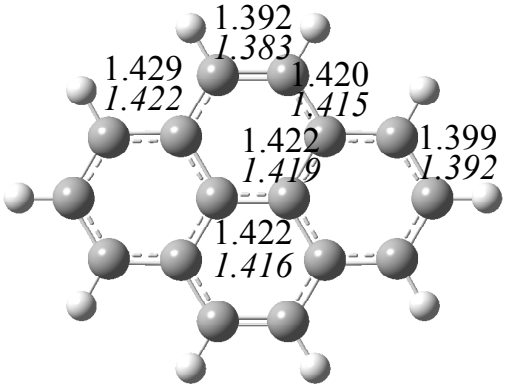
[a] Conical intersections were optimized using CASSCF(13,14)/6-31G* level.

Table S4. CASPT2/6-31G* energies (a.u.) of states D_0, D_1, and D_2 at the PES minima and at the D_0/D_1 and D_1/D_2 conical intersections.

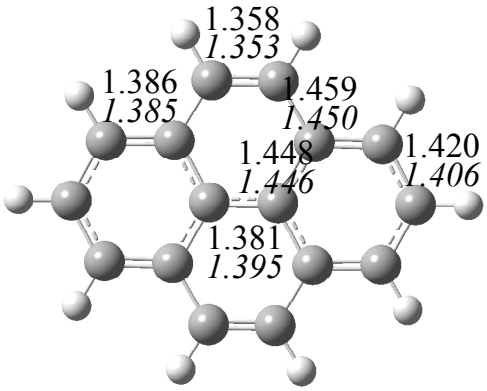
Geometry/State	B_{2g} energy	B_{3g} energy	B_{1u} energy
D_0 minimum	-613.543893	-613.506146	-613.486188
D_1 minimum	-613.533541	-613.514582	-613.478940
D_2 minimum	-613.540449	-613.505953	-613.490503
D_0/D_1 CI	-613.515262	-613.505066	
D_1/D_2 CI		-613.468592	-613.478623

Figure S1. MMVB and CASSCF (in italics) optimized structures. Bond lengths are in Å.

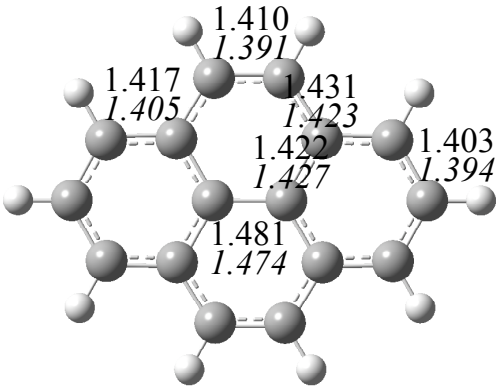
$D_0(B_{2g})$ D_{2h} minimum



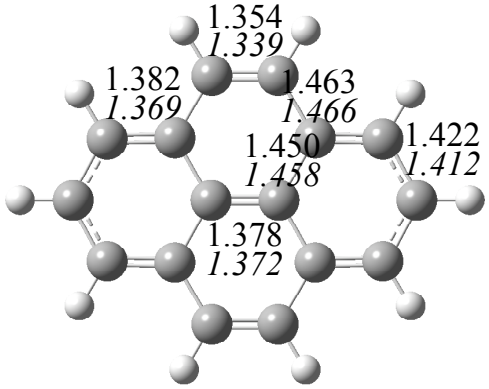
$D_1(B_{3g})$ D_{2h} minimum



$D_2(B_{1u})$ D_{2h} minimum



D_0/D_1 D_{2h} conical intersection



D_1/D_2 D_{2h} conical intersection