Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Radical cation ($C^{\bullet+}$–π) and radical anion ($A^{\bullet-}$–π) interactions with aromatic rings: Energetic, Orbitalic and Spin density considerations.

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Cartesian Coordinates

1

Energy = -287.2939055071

N	-0.0000001	-0.0000044	2.3345594
H	-0.0000001	0.9556900	1.9542973
H	-0.8276566	-0.4778521	1.9543004
H	0.8276562	-0.4778522	1.9543004
C	0.0000000	1.4121170	-0.5570802
C	1.2231311	0.7061769	-0.5578585
C	1.2229273	-0.7060555	-0.5570811
C	0.0000001	-1.4123497	-0.5578471
C	-1.2229271	-0.7060554	-0.5570823
C	-1.2231311	0.7061770	-0.5578572
H	0.0000001	2.5058880	-0.5968166
H	2.1703601	1.2530598	-0.5924545
H	2.1701608	-1.2529410	-0.5968131
H	0.0000001	-2.5061168	-0.5924407
H	-2.1701606	-1.2529410	-0.5968140
H	-2.1703601	1.2530599	-0.5924528
H	-0.0000001	-0.0000003	3.3585430

2

Energy = -307.0720724348

H	-0.4477006	0.7754402	-1.7132581
H	-0.4477006	-0.7754402	-1.7132581
H	0.8954012	0.0000000	-1.7132581
C	-1.4143230	0.0000000	0.5894983
C	-0.7071889	-1.2248871	0.5871480
C	0.7071615	-1.2248396	0.5894983
C	1.4143778	0.0000000	0.5871480
C	0.7071615	1.2248396	0.5894983
C	-0.7071889	1.2248871	0.5871480
H	-2.5081509	0.0000000	0.6221825
H	-1.2540188	-2.1720243	0.6284945
H	1.2540755	-2.1721224	0.6221825
H	2.5080376	0.0000000	0.6284945
H	1.2540755	2.1721224	0.6221825
H	-1.2540188	2.1720243	0.6284945
O	0.0000000	0.0000000	-2.1421956

3

16

Energy = -287.5912180356

N	0.0000000	0.0000000	2.2120000
H	0.0000000	0.9556900	1.9542973
H	-0.8276566	-0.4778521	1.9543004

H	0.8276562	-0.4778522	1.9543004
C	0.0000000	1.4121170	-0.5570802
C	1.2231311	0.7061769	-0.5578585
C	1.2229273	-0.7060555	-0.5570811
C	0.0000000	-1.4123497	-0.5578471
C	-1.2229271	-0.7060554	-0.5570823
C	-1.2231311	0.7061770	-0.5578572
H	0.0000000	2.5058880	-0.5968166
H	2.1703601	1.2530598	-0.5924545
H	2.1701608	-1.2529410	-0.5968131
H	0.0000000	-2.5061168	-0.5924407
H	-2.1701606	-1.2529410	-0.5968140
H	-2.1703601	1.2530599	-0.5924528

4

Energy = -306.3152968826

H	0.0000000	0.7656524	-2.2144860
H	0.0000000	-0.7656524	-2.2144860
C	-1.2447137	-0.7273600	0.6013632
C	0.0000000	-1.3371528	0.6048583
C	1.2447137	-0.7273600	0.6013632
C	1.2447137	0.7273600	0.6013632
C	0.0000000	1.3371528	0.6048583
C	-1.2447137	0.7273600	0.6013632
H	-2.2256953	-1.2183411	0.5937980
H	0.0000000	-2.4620814	0.6206193
H	2.2256953	-1.2183411	0.5937980
H	2.2256953	1.2183411	0.5937980
H	0.0000000	2.4620814	0.6206193
H	-2.2256953	1.2183411	0.5937980
O	0.0000000	0.0000000	-2.8026282

5

Energy = -286.6556002684

N	-2.0220944	-0.9350632	0.0000000
H	-2.2065026	-1.5358075	0.8074999
H	-2.7935972	-0.2633696	0.0000000
H	-2.2065026	-1.5358075	-0.8074999
C	1.0726023	-0.3065466	1.1952534
C	1.3803277	-0.9535247	0.0000000
C	1.0726023	-0.3065466	-1.1952534
C	0.4610439	1.0161989	-1.1952957
C	0.1673743	1.6696291	0.0000000
C	0.4610439	1.0161989	1.1952957
H	1.2887505	-0.7806978	2.1569567
H	1.8432571	-1.9418480	0.0000000
H	1.2887505	-0.7806978	-2.1569567
H	0.2391240	1.4875916	-2.1570289
H	-0.2853037	2.6626993	0.0000000
H	0.2391240	1.4875916	2.1570289

6

Energy = -306.3300088843

H	0.0000000	0.7560482	-2.8415005
H	0.0000000	-0.7560482	-2.8415005
C	-1.1802512	-0.6851237	0.6593123
C	0.0000000	-1.4824130	0.6608245
C	1.1802512	-0.6851237	0.6593123
C	1.1802512	0.6851237	0.6593123
C	0.0000000	1.4824130	0.6608245
C	-1.1802512	0.6851237	0.6593123

H -2.1105929 -1.2957629 0.6570685
H 0.0000000 -2.5726452 0.6663179
H 2.1105929 -1.2957629 0.6570685
H 2.1105929 1.2957629 0.6570685
H 0.0000000 2.5726452 0.6663179
H -2.1105929 1.2957629 0.6570685
O 0.0000000 0.0000000 -2.2368071

7

Energy = -938.3043398807
C -0.0000005 -0.0000060 -3.4964048
H -0.0000001 1.0286241 -3.9660998
H 0.8908348 -0.5143460 -3.9660462
O -0.0000017 0.0000459 -2.1258128
H -0.8908351 -0.5143459 -3.9660476
C -1.2084701 0.6977197 0.4518082
C -0.0000080 1.3955800 0.4521956
C 1.2084817 0.6977154 0.4518080
C 1.2086050 -0.6977854 0.4522050
C 0.0000055 -1.3954415 0.4518428
C -1.2086122 -0.6977850 0.4522046
F -2.3809777 1.3746625 0.4155694
F 0.0000004 2.7494474 0.4155251
F 2.3809766 1.3746617 0.4155708
F 2.3810942 -1.3747194 0.4154408
F 0.0000001 -2.7493083 0.4155528
F -2.3810929 -1.3747191 0.4154396

8

Energy = -1261.018262844
C -0.6988042 1.2103644 1.4118861
C -1.3976152 0.0000000 1.4119228
C -0.6988042 -1.2103644 1.4118861
C 0.6988076 -1.2103703 1.4119228
C 1.3976084 0.0000000 1.4118861
C 0.6988076 1.2103703 1.4119228
F -1.3743041 2.3803645 1.3930062
F -2.7486392 0.0000000 1.3927873
F -1.3743041 -2.3803645 1.3930062
F 1.3743196 -2.3803914 1.3927873
F 2.7486082 0.0000000 1.3930062
F 1.3743196 2.3803914 1.3927873
C 0.0000000 0.0000000 -3.4915352
H 0.5144503 0.8910541 -3.8958091
H -1.0289007 0.0000000 -3.8958091
H 0.5144503 -0.8910541 -3.8958091
S 0.0000000 0.0000000 -1.6498444

9

Energy = -937.7032409925
C 0.6982607 1.2091983 0.9768784
C 1.3963602 0.0000000 0.9783600
C 0.6982607 -1.2091983 0.9768784
C -0.6982607 -1.2091983 0.9768784
C -1.3963602 0.0000000 0.9783600
C -0.6982607 1.2091983 0.9768784
F 1.3747958 -2.3807022 0.9527939
F 2.7492311 0.0000000 0.9530083
F 1.3747958 2.3807022 0.9527939
F -1.3747958 2.3807022 0.9527939
F -2.7492311 0.0000000 0.9530083

```
F    -1.3747958   -2.3807022    0.9527939
C     0.0000000    0.0000000   -2.9313041
H    -0.9423412    0.0000000   -3.5135441
O     0.0000000    0.0000000   -1.6230337
H     0.9423412    0.0000000   -3.5135441
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10

```
Energy = -1260.404890571
C     0.6990393    1.2105087    1.1705633
C     1.3980984    0.0000000    1.1710849
C     0.6990393   -1.2105087    1.1705633
C    -0.6990393   -1.2105087    1.1705633
C    -1.3980984    0.0000000    1.1710849
C    -0.6990393    1.2105087    1.1705633
F     1.3742038   -2.3802380    1.1548058
F     2.7484670    0.0000000    1.1546737
F     1.3742038    2.3802380    1.1548058
F    -1.3742038    2.3802380    1.1548058
F    -2.7484670    0.0000000    1.1546737
F    -1.3742038   -2.3802380    1.1548058
C     0.0000000    0.0000000   -3.6343377
H    -0.9366168    0.0000000   -4.2029388
H     0.9366168    0.0000000   -4.2029388
S     0.0000000    0.0000000   -1.9127780
```

11

```
Energy = -1013.380638128
C     0.0000000    0.0000000   -2.4444846
C     0.0000000   -0.7416491   -3.6603624
C     0.0000000    0.7416491   -3.6603624
H     0.0000000    1.6524190   -4.2484213
H     0.0000000   -1.6524190   -4.2484213
O     0.0000000    0.0000000   -1.1848991
C    -1.2163079   -0.7019568    1.6065064
C     0.0000000   -1.4045143    1.6177854
C     1.2163079   -0.7019568    1.6065064
C     1.2163079    0.7019568    1.6065064
C     0.0000000    1.4045143    1.6177854
C    -1.2163079    0.7019568    1.6065064
F     0.0000000   -2.7577116    1.6210247
F    -2.3891406   -1.3780071    1.6358263
F    -2.3891406    1.3780071    1.6358263
F     2.3891406    1.3780071    1.6358263
F     2.3891406   -1.3780071    1.6358263
F     0.0000000    2.7577116    1.6210247
```

12

```
Energy = -1336.057160646
C     0.0000000    0.0000000   -2.9476384
C     0.0000000   -0.7357190   -4.1411532
C     0.0000000    0.7357190   -4.1411532
H     0.0000000    1.6898914   -4.6555882
H     0.0000000   -1.6898914   -4.6555882
C    -1.2108518   -0.6994249    1.8224935
C     0.0000000   -1.3990807    1.8238604
C     1.2108518   -0.6994249    1.8224935
C     1.2108518    0.6994249    1.8224935
C     0.0000000    1.3990807    1.8238604
C    -1.2108518    0.6994249    1.8224935
F     0.0000000   -2.7483056    1.8099956
F    -2.3799590   -1.3738848    1.8093829
```

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F    -2.3799590    1.3738848    1.8093829
F     2.3799590    1.3738848    1.8093829
F     2.3799590   -1.3738848    1.8093829
F     0.0000000    2.7483056    1.8099956
S     0.0000000    0.0000000   -1.2540964
```

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```
Energy = -1090.391210941
C    -1.2094940   -0.6985587    2.3312156
C    -1.2094940    0.6985587    2.3312156
C     0.0000000    1.3971308    2.3326778
C     1.2094940    0.6985587    2.3312156
C     1.2094940   -0.6985587    2.3312156
C     0.0000000   -1.3971308    2.3326778
F     0.0000000    2.7491137    2.3105175
F    -2.3805751    1.3744231    2.3104121
F    -2.3805751   -1.3744231    2.3104121
F     0.0000000   -2.7491137    2.3105175
F     2.3805751   -1.3744231    2.3104121
F     2.3805751    1.3744231    2.3104121
C     0.0000000    0.0000000   -1.5674534
C     0.0000000    1.1742734   -2.4533980
H     0.0000000    2.2085628   -2.0985634
C     0.0000000    0.7325811   -3.7766904
H     0.0000000    1.3596596   -4.6739930
C     0.0000000   -1.1742734   -2.4533980
H     0.0000000   -2.2085628   -2.0985634
C     0.0000000   -0.7325811   -3.7766904
H     0.0000000   -1.3596596   -4.6739930
O     0.0000000    0.0000000   -0.2801584
```

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```
C    -1.2109925   -0.6997600    2.7091974
C    -1.2109925    0.6997600    2.7091974
C     0.0000000    1.3998373    2.7109170
C     1.2109925    0.6997600    2.7091974
C     1.2109925   -0.6997600    2.7091974
C     0.0000000   -1.3998373    2.7109170
F     0.0000000    2.7480639    2.6973458
F    -2.3796617    1.3735367    2.6968364
F    -2.3796617   -1.3735367    2.6968364
F     0.0000000   -2.7480639    2.6973458
F     2.3796617   -1.3735367    2.6968364
F     2.3796617    1.3735367    2.6968364
C     0.0000000    0.0000000   -2.0853283
C     0.0000000    1.1665763   -2.9450081
H     0.0000000    2.1980459   -2.5832774
C     0.0000000    0.7135119   -4.2816874
H     0.0000000    1.3527414   -5.1708252
C     0.0000000   -1.1665763   -2.9450081
H     0.0000000   -2.1980459   -2.5832774
C     0.0000000   -0.7135119   -4.2816874
H     0.0000000   -1.3527414   -5.1708252
S     0.0000000    0.0000000   -0.3937364
```