SUPPORTING INFORMATION

Theoretical Prediction of Benzyne-like Species in Pyrene Diradicals

I. García-Cruz,[a*] J. M. Martínez-Magadán,[a] J. M. Bofill[b] and F. Illas[a,c]

a) Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, Colonia San Bartolo Atepehuacán, México D. F., 07730, México
b) Departament de Química Orgànica i Centre especial de Recerca en Química Teòrica, Universitat de Barcelona i Parc Científic de Barcelona, C/ Martí i Franquès 1, 08028 Barcelona, Spain
c) Departament de Química Física i Centre especial de Recerca en Química Teòrica, Universitat de Barcelona i Parc Científic de Barcelona, C/ Martí i Franquès 1, 08028 Barcelona, Spain.

Cartesian coordinates of the B3LYP/6-31++G** optimized geometries for electronic ground state of pyrene

C	-3.063420	0.000003	0.352603
C	-3.063768	0.000002	1.747930
C	-1.862421	0.000003	2.457666
C	-0.629260	0.000002	1.783222
C	0.629988	0.000001	2.479446
C	1.813951	-0.000001	1.804005
C	1.855337	-0.000001	0.365762
C	3.063420	-0.000003	-0.352603
C	3.063768	-0.000005	-1.747930
C	1.862421	-0.000003	-2.457666
C	0.629260	-0.000001	-1.783222
C	-0.629988	-0.000001	-2.479446
C	-1.813951	0.000001	-1.804005
C	-1.855337	0.000002	-0.365762
C	-0.620142	0.000001	0.353815
C	0.620142	-0.000001	-0.353815
H	-4.003796	0.000004	-0.192360
H	-4.007192	0.000003	2.286243
H	-1.871744	0.000004	3.544517
H	0.618291	0.000001	3.566351
H	2.755636	-0.000001	2.346910
H	4.003796	-0.000003	0.192360
H	4.007192	-0.000007	-2.286243
H	1.871744	-0.000003	-3.544517
H	-0.618291	-0.000001	-3.566351
H	-2.755636	0.000002	-2.346910

Cartesian coordinates of the B3LYP/6-31++G** optimized geometries for electronic ground state of the hydrogen molecule

H	0.000000	0.000000	-0.371893
H	0.000000	0.000000	0.371893

Cartesian coordinates of the B3LYP/6-31++G** optimized geometries for electronic ground state of the C_1 pyrene radical

C	0.654488	0.000000	-1.814846
C	0.661913	0.000000	-0.383031
C	1.899623	0.000000	0.336804
C	3.116254	0.000000	-0.383976
C	3.035805	0.000000	-1.756795
C	1.885585	0.000000	-2.510578
H	1.899905	0.000000	-3.597189
H	4.065525	0.000000	0.144997
C	1.865581	0.000000	1.774646
C	0.683596	0.000000	2.453646
C	-0.577279	0.000000	1.762179
C	-0.574745	0.000000	0.332611
C	-1.815481	0.000000	-0.377509
C	-1.786755	0.000000	-1.815256
C	-0.609114	0.000000	-2.501760
H	-0.606181	0.000000	-3.588434
H	-2.732560	0.000000	-2.350908
C	-3.019266	0.000000	0.348084
C	-3.012272	0.000000	1.743181
C	-1.806189	0.000000	2.444385
H	-1.808264	0.000000	3.531179
H	-3.952289	0.000000	2.287138
H	-3.962606	0.000000	-0.191587
H	0.676781	0.000000	3.540586
H	2.809224	0.000000	2.313515

Cartesian coordinates of the B3LYP/6-31G** optimized geometries for electronic ground state of the C_2 pyrene radical

C	0.622403	0.000000	-1.829557
C	0.633652	0.000000	-0.392380
C	1.877346	0.000000	0.315112
C	3.086434	0.000000	-0.403746
C	3.090456	0.000000	-1.807349
C	1.867829	0.000000	-2.438896
H	4.025429	0.000000	-2.359992
H	4.029310	0.000000	0.137908
C	1.843670	0.000000	1.754052
C	0.664176	0.000000	2.437482
C	-0.600085	0.000000	1.750714
C	-0.602372	0.000000	0.321213
C	-1.841872	0.000000	-0.391097
C	-1.813730	0.000000	-1.830305
C	-0.639021	0.000000	-2.521566
H	-0.631406	0.000000	-3.606907
H	-2.760776	0.000000	-2.363516
C	-3.044595	0.000000	0.335742
C	-3.034786	0.000000	1.731191
C	-1.828964	0.000000	2.433162
H	-1.831519	0.000000	3.519937
H	-3.974518	0.000000	2.275775
H	-3.988868	0.000000	-0.202187
H	0.661131	0.000000	3.524273
H	2.787977	0.000000	2.292081

Cartesian coordinates of the B3LYP/6-31G** optimized geometries for electronic ground state of the C_4 pyrene radical

C	0.627633	0.000000	-1.830215
C	0.613144	0.000000	-0.393228
C	1.852782	0.000000	0.317333
C	3.057067	0.000000	-0.407798
C	3.055125	0.000000	-1.803305
C	1.854559	0.000000	-2.514363
H	1.854299	0.000000	-3.599632
H	3.998062	0.000000	-2.342110
H	3.999212	0.000000	0.133869
C	1.818489	0.000000	1.755853
C	0.637375	0.000000	2.435759
C	-0.626068	0.000000	1.746816
C	-0.627850	0.000000	0.317087
C	-1.873730	0.000000	-0.387658
C	-1.848451	0.000000	-1.837702
C	-0.650198	0.000000	-2.446715
H	-2.787178	0.000000	-2.386232
C	-3.074752	0.000000	0.340195
C	-3.060413	0.000000	1.735995
C	-1.852740	0.000000	2.433513
H	-1.851339	0.000000	3.520202
H	-3.998747	0.000000	2.283088
H	-4.019985	0.000000	-0.195713
H	0.631325	0.000000	3.522580
H	2.762517	0.000000	2.294542

Cartesian coordinates of the B3LYP/6-31G** optimized geometries for lowest singlet state of the (C_1,C_2) compound. This is a closed shell electronic state.

C	-3.033272	0.000000	-1.702966
C	-3.050366	0.000000	-0.453628
C	-1.949367	0.000000	0.399931
C	-1.904464	0.000000	1.828290
C	-0.705171	0.000000	2.479925
C	0.540451	0.000000	1.764599
C	1.777371	0.000000	2.434986
C	2.975701	0.000000	1.723921
C	2.968924	0.000000	0.328082
C	1.760208	0.000000	-0.387081
C	1.721675	0.000000	-1.823955
C	0.540742	0.000000	-2.502658
C	-0.725568	0.000000	-1.816341
C	-1.943893	0.000000	-2.552649
C	-0.720129	0.000000	-0.371880
C	0.523157	0.000000	0.332906
H	-2.840292	0.000000	2.377315
H	-0.674447	0.000000	3.566258
H	1.788543	0.000000	3.521590
H	3.920809	0.000000	2.258873
H	3.907135	0.000000	-0.220275
H	2.663271	0.000000	-2.366543
H	0.534350	0.000000	-3.589227
H	-1.955362	0.000000	-3.636887

Cartesian coordinates of the B3LYP/6-31G** optimized geometries for lowest singlet state of the (C_1,C_4) compound. This is a broken symmetry open shell singlet state

C	-3.177951	0.000000	-1.533880
C	-3.176725	0.000000	-0.158693
C	-1.913773	0.000000	0.479427
C	-1.717509	0.000000	1.880481
C	-0.545199	0.000000	2.538531
C	0.672864	0.000000	1.752466
C	1.944514	0.000000	2.348350
C	3.098661	0.000000	1.563509
C	3.008604	0.000000	0.172087
C	1.756869	0.000000	-0.468043
C	1.633004	0.000000	-1.900857
C	0.413969	0.000000	-2.510451
C	-0.802231	0.000000	-1.742972
C	-2.076469	0.000000	-2.357186
C	-0.713010	0.000000	-0.315008
C	0.566616	0.000000	0.324638
H	-4.086212	0.000000	0.433069
H	-0.478421	0.000000	3.623715
H	2.021935	0.000000	3.432132
H	4.074061	0.000000	2.041196
H	3.911652	0.000000	-0.432336
H	2.541917	0.000000	-2.496779
H	0.340337	0.000000	-3.594625
H	-2.158668	0.000000	-3.440765

Cartesian coordinates of the B3LYP/6-31G** optimized geometries for lowest singlet state of the (C_1,C_5) compound. This is a broken symmetry open shell singlet state

C	-3.143097	0.000000	-1.530822
C	-3.147427	0.000000	-0.156100
C	-1.889051	0.000000	0.487763
C	-1.774692	0.000000	1.934171
C	-0.539075	0.000000	2.460446
C	0.696119	0.000000	1.764556
C	1.962398	0.000000	2.372354
C	3.117594	0.000000	1.590038
C	3.033141	0.000000	0.197434
C	1.786653	0.000000	-0.452974
C	1.667468	0.000000	-1.886148
C	0.448148	0.000000	-2.495163
C	-0.770070	0.000000	-1.730535
C	-2.040906	0.000000	-2.351406
C	-0.691300	0.000000	-0.300880
C	0.591959	0.000000	0.330909
H	-4.062501	0.000000	0.429567
H	-2.677691	0.000000	2.539173
H	2.028075	0.000000	3.455646
H	4.091579	0.000000	2.070177
H	3.940006	0.000000	-0.401394
H	2.577421	0.000000	-2.480596
H	0.375716	0.000000	-3.579345
H	-2.119780	0.000000	-3.435083

Cartesian coordinates of the B3LYP/6-31G** optimized geometries for lowest singlet state of the (C_1,C_7) compound. This is a broken symmetry open shell singlet state

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.375252
C	1.256498	0.000000	2.023835
C	1.372081	0.000000	3.457891
C	2.587945	0.000000	4.074094
C	3.802914	0.000000	3.305191
C	5.082384	0.000000	3.839356
C	6.265768	0.000000	3.137441
C	6.176850	0.000000	1.737000
C	4.927010	0.000000	1.091136
C	4.811279	0.000000	-0.342579
C	3.595007	0.000000	-0.958401
C	2.373759	0.000000	-0.199306
C	1.103328	0.000000	-0.820694
C	2.449063	0.000000	1.230746
C	3.726085	0.000000	1.869897
H	-0.916539	0.000000	1.959017
H	0.459730	0.000000	4.047982
H	2.662694	0.000000	5.156909
H	7.231966	0.000000	3.633275
H	7.085356	0.000000	1.139519
H	5.722923	0.000000	-0.934268
H	3.528656	0.000000	-2.042919
H	1.024972	0.000000	-1.904529

Cartesian coordinates of the B3LYP/6-31G** optimized geometries for lowest singlet state of the (C_1,C_8) compound. This is a broken symmetry open shell singlet state

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.374830
C	1.256035	0.000000	2.024618
C	1.368884	0.000000	3.457544
C	2.586001	0.000000	4.071341
C	3.805277	0.000000	3.310281
C	5.074455	0.000000	3.934134
C	6.180048	0.000000	3.116844
C	6.180048	0.000000	1.742103
C	4.924053	0.000000	1.092142
C	4.810981	0.000000	-0.340734
C	3.593954	0.000000	-0.954512
C	2.374580	0.000000	-0.193361
C	1.105512	0.000000	-0.817270
C	2.451638	0.000000	1.236502
C	3.728497	0.000000	1.880372
H	-0.916612	0.000000	1.958596
H	0.456457	0.000000	4.047820
H	2.653515	0.000000	5.155927
H	5.150147	0.000000	5.018208
H	7.096626	0.000000	1.158156
H	5.723371	0.000000	-0.931075
H	3.526154	0.000000	-2.039108
H	1.030065	0.000000	-1.901382

Cartesian coordinates of the B3LYP/6-31G** optimized geometries for lowest singlet state of the (C_2,C_4) compound. This is a broken symmetry open shell singlet state

C	-0.014561	0.000000	0.030268
C	0.002305	0.000000	1.405697
C	1.127545	0.000000	2.214552
C	1.209574	0.000000	3.631745
C	2.327257	0.000000	4.376431
C	3.608341	0.000000	3.698159
C	4.824533	0.000000	4.399210
C	6.040164	0.000000	3.713232
C	6.067726	0.000000	2.319338
C	4.874618	0.000000	1.575564
C	4.871224	0.000000	0.137492
C	3.706664	0.000000	-0.569324
C	2.427862	0.000000	0.091232
C	1.221555	0.000000	-0.631486
C	2.401501	0.000000	1.522068
C	3.622305	0.000000	2.267246
H	-0.944880	0.000000	-0.530187
H	2.302254	0.000000	5.463403
H	4.810622	0.000000	5.485600
H	6.972044	0.000000	4.271167
H	7.018386	0.000000	1.793026
H	5.826482	0.000000	-0.380610
H	3.724471	0.000000	-1.655887
H	1.252418	0.000000	-1.718192

Cartesian coordinates of the B3LYP/6-31G** optimized geometries for lowest singlet state of the (C_2,C_5) compound. This is a broken symmetry open shell singlet state

C	-3.044632	0.000000	-1.869804
C	-3.039704	0.000000	-0.492866
C	-1.928815	0.000000	0.327498
C	-1.962495	0.000000	1.780309
C	-0.784872	0.000000	2.427752
C	0.515039	0.000000	1.858092
C	1.714775	0.000000	2.587760
C	2.941776	0.000000	1.922573
C	2.997822	0.000000	0.528653
C	1.822223	0.000000	-0.242813
C	1.842677	0.000000	-1.681324
C	0.689010	0.000000	-2.407071
C	-0.601413	0.000000	-1.769288
C	-1.797282	0.000000	-2.511583
C	-0.652829	0.000000	-0.339200
C	0.556657	0.000000	0.420927
H	-3.965814	0.000000	-2.445170
H	-2.921374	0.000000	2.288763
H	1.673637	0.000000	3.672221
H	3.863252	0.000000	2.497234
H	3.960118	0.000000	0.023745
H	2.806429	0.000000	-2.183517
H	0.726348	0.000000	-3.493197
H	-1.750222	0.000000	-3.597764

Cartesian coordinates of the B3LYP/6-31G** optimized geometries for lowest singlet state of the (C_2,C_7) compound. This is a broken symmetry open shell singlet state

C	-0.003022	0.000000	0.000635
C	-0.015842	0.000000	1.376484
C	1.090480	0.000000	2.213143
C	1.039294	0.000000	3.650918
C	2.181768	0.000000	4.394565
C	3.475757	0.000000	3.765627
C	4.688649	0.000000	4.438538
C	5.941499	0.000000	3.869796
C	6.010638	0.000000	2.467862
C	4.840468	0.000000	1.687236
C	4.880355	0.000000	0.248131
C	3.737961	0.000000	-0.495378
C	2.438298	0.000000	0.123897
C	1.250906	0.000000	-0.630186
C	2.367389	0.000000	1.552762
C	3.562633	0.000000	2.330773
H	-0.917646	0.000000	-0.585061
H	0.065569	0.000000	4.130313
H	2.137538	0.000000	5.478993
H	6.847333	0.000000	4.468995
H	6.980402	0.000000	1.976304
H	5.851096	0.000000	-0.240288
H	3.791438	0.000000	-1.580741
H	1.308081	0.000000	-1.715903

Cartesian coordinates of the B3LYP/6-31G** optimized geometries for lowest singlet state of the (C_2,C_8) compound. This is a broken symmetry open shell singlet state

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.375873
C	1.112399	0.000000	2.203430
C	1.071908	0.000000	3.640443
C	2.222496	0.000000	4.371304
C	3.514634	0.000000	3.738712
C	4.713708	0.000000	4.488093
C	5.896135	0.000000	3.785824
C	6.038683	0.000000	2.418092
C	4.855971	0.000000	1.643056
C	4.885159	0.000000	0.205311
C	3.734686	0.000000	-0.525900
C	2.442697	0.000000	0.106619
C	1.249445	0.000000	-0.638544
C	2.386245	0.000000	1.536686
C	3.587610	0.000000	2.308245
H	-0.919516	0.000000	-0.577888
H	0.102831	0.000000	4.129428
H	2.180635	0.000000	5.457039
H	4.680069	0.000000	5.574201
H	7.010851	0.000000	1.932560
H	5.851519	0.000000	-0.291459
H	3.777771	0.000000	-1.611867
H	1.299375	0.000000	-1.724711

Cartesian coordinates of the B3LYP/6-31G** optimized geometries for lowest singlet state of the (C_2,C_9) compound. This is a broken symmetry open shell singlet state

C	-2.983900	0.000000	-1.916618
C	-2.983653	0.000000	-0.540673
C	-1.870940	0.000000	0.286447
C	-1.904548	0.000000	1.724373
C	-0.750788	0.000000	2.450195
C	0.541735	0.000000	1.815911
C	1.735993	0.000000	2.558950
C	2.983902	0.000000	1.916623
C	2.983633	0.000000	0.540624
C	1.870909	0.000000	-0.286407
C	1.904553	0.000000	-1.724410
C	0.750821	0.000000	-2.450189
C	-0.541777	0.000000	-1.815853
C	-1.735953	0.000000	-2.558987
C	-0.599850	0.000000	-0.385739
C	0.599861	0.000000	0.385752
H	-3.904310	0.000000	-2.493245
H	-2.871469	0.000000	2.217207
H	-0.790729	0.000000	3.536170
H	1.688914	0.000000	3.645162
H	3.904324	0.000000	2.493201
H	2.871541	0.000000	-2.217116
H	0.790595	0.000000	-3.536164
H	-1.688863	0.000000	-3.645208

Cartesian coordinates of the B3LYP/6-31G** optimized geometries for lowest singlet state of the (C_2,C_{11}) compound. This is a broken symmetry open shell singlet state

C	-2.992572	0.000000	-1.948581
C	-2.993878	0.000000	-0.573416
C	-1.880745	0.000000	0.253585
C	-1.922678	0.000000	1.691576
C	-0.774117	0.000000	2.425038
C	0.520747	0.000000	1.796621
C	1.715638	0.000000	2.537234
C	2.956366	0.000000	1.898726
C	3.042636	0.000000	0.506027
C	1.875091	0.000000	-0.274811
C	1.840813	0.000000	-1.692958
C	0.752219	0.000000	-2.481449
C	-0.551783	0.000000	-1.844769
C	-1.743172	0.000000	-2.590094
C	-0.606405	0.000000	-0.412772
C	0.589541	0.000000	0.369101
H	-3.911878	0.000000	-2.526926
H	-2.893032	0.000000	2.177776
H	-0.819212	0.000000	3.510866
H	1.663835	0.000000	3.622682
H	3.865719	0.000000	2.492381
H	4.008781	0.000000	0.011751
H	0.813750	0.000000	-3.566812
H	-1.694169	0.000000	-3.676073

Cartesian coordinates of the B3LYP/6-31G** optimized geometries for lowest singlet state of the (C_2,C_{14}) compound. This is a closed shell electronic state..

C	0.698062	0.000000	-1.771415
C	0.613986	0.000000	-0.349019
C	1.879124	0.000000	0.306459
C	1.882429	0.000000	1.748267
C	0.698432	0.000000	2.435522
C	-0.586986	0.000000	1.772402
C	-0.610024	0.000000	0.346752
C	-1.823181	0.000000	-0.402413
C	-1.735313	0.000000	-1.846143
C	-0.539098	0.000000	-2.511899
H	-0.511089	0.000000	-3.596693
H	-2.663057	0.000000	-2.412103
C	-3.030538	0.000000	0.316966
C	-3.018349	0.000000	1.715696
C	-1.822781	0.000000	2.441763
H	-1.848551	0.000000	3.528073
H	-3.962837	0.000000	2.252543
H	-3.977087	0.000000	-0.216678
H	0.710072	0.000000	3.522198
H	2.828843	0.000000	2.279188
C	2.948502	0.000000	-0.571261
C	3.308560	0.000000	-1.880571
C	1.999327	0.000000	-2.241171
H	4.250792	0.000000	-2.416140

Cartesian coordinates of the B3LYP/6-31G** optimized geometries for lowest singlet state of the (C_4,C_5) compound. This is a closed shell electronic state.

C	-3.129699	0.000000	-1.689735
C	-3.152499	0.000000	-0.291256
C	-1.953757	0.000000	0.423510
C	-1.727884	0.000000	1.826362
C	-0.650317	0.000000	2.428569
C	0.662926	0.000000	1.886014
C	1.899931	0.000000	2.532397
C	3.079126	0.000000	1.780217
C	3.033962	0.000000	0.389076
C	1.807028	0.000000	-0.303606
C	1.753188	0.000000	-1.741230
C	0.564594	0.000000	-2.405526
C	-0.688210	0.000000	-1.698195
C	-1.921101	0.000000	-2.380236
C	-0.674504	0.000000	-0.269470
C	0.582931	0.000000	0.433287
H	-4.065082	0.000000	-2.241279
H	-4.093470	0.000000	0.248556
H	1.933366	0.000000	3.616715
H	4.038927	0.000000	2.288081
H	3.957653	0.000000	-0.183216
H	2.690570	0.000000	-2.291024
H	0.541705	0.000000	-3.492007
H	-1.917952	0.000000	-3.466895

Cartesian coordinates of the B3LYP/6-31G** optimized geometries for lowest singlet state of the (C_4,C_{11}) compound. This is a broken symmetry open shell singlet state

C	-3.079156	0.000000	-1.743589
C	-3.079706	0.000000	-0.348846
C	-1.866221	0.000000	0.359098
C	-1.751433	0.000000	1.772965
C	-0.621011	0.000000	2.499217
C	0.643969	0.000000	1.788331
C	1.879397	0.000000	2.456916
C	3.079162	0.000000	1.743531
C	3.079755	0.000000	0.348836
C	1.866193	0.000000	-0.359095
C	1.751432	0.000000	-1.772937
C	0.620976	0.000000	-2.499181
C	-0.643959	0.000000	-1.788298
C	-1.879410	0.000000	-2.456959
C	-0.619725	0.000000	-0.358287
C	0.619735	0.000000	0.358305
H	-4.022817	0.000000	-2.281070
H	-4.013497	0.000000	0.203999
H	-0.618605	0.000000	3.586358
H	1.892663	0.000000	3.543367
H	4.022766	0.000000	2.281141
H	4.013488	0.000000	-0.204092
H	0.618572	0.000000	-3.586335
H	-1.892557	0.000000	-3.543425

Cartesian coordinates of the B3LYP/6-31G** optimized geometries for lowest singlet state of the (C_4,C_{12}) compound. This is a broken symmetry open shell singlet state

C	-3.104941	0.000000	-1.760677
C	-3.104493	0.000000	-0.365227
C	-1.893285	0.000000	0.346537
C	-1.774816	0.000000	1.759727
C	-0.642248	0.000000	2.482805
C	0.622105	0.000000	1.772008
C	1.855031	0.000000	2.444832
C	3.054115	0.000000	1.731696
C	3.050432	0.000000	0.336687
C	1.839952	0.000000	-0.375993
C	1.800815	0.000000	-1.825815
C	0.598751	0.000000	-2.426478
C	-0.674677	0.000000	-1.802465
C	-1.907415	0.000000	-2.476714
C	-0.644932	0.000000	-0.365741
C	0.600983	0.000000	0.340789
H	-4.049609	0.000000	-2.296099
H	-4.039100	0.000000	0.186429
H	-0.639199	0.000000	3.569883
H	1.866540	0.000000	3.531207
H	3.999004	0.000000	2.267561
H	3.988508	0.000000	-0.211355
H	2.735139	0.000000	-2.381479
H	-1.913538	0.000000	-3.561967

Cartesian coordinates of the B3LYP/6-31G** optimized geometries of the (C_1,C_2) compound in the lowest triplet state

C	0.675219	0.000000	-1.850356
C	0.679379	0.000000	-0.411120
C	1.914599	0.000000	0.309027
C	3.135379	0.000000	-0.407671
C	3.108939	0.000000	-1.784828
C	1.906754	0.000000	-2.494043
H	4.081523	0.000000	0.130170
C	1.874767	0.000000	1.745966
C	0.689484	0.000000	2.420486
C	-0.568419	0.000000	1.724777
C	-0.561141	0.000000	0.295284
C	-1.797470	0.000000	-0.422447
C	-1.762280	0.000000	-1.861529
C	-0.586165	0.000000	-2.548424
H	-0.573521	0.000000	-3.633444
H	-2.706325	0.000000	-2.400075
C	-3.003709	0.000000	0.296913
C	-3.003021	0.000000	1.692963
C	-1.801699	0.000000	2.400719
H	-1.809606	0.000000	3.487429
H	-3.945857	0.000000	2.231953
H	-3.944486	0.000000	-0.247027
H	0.678940	0.000000	3.507234
H	2.815638	0.000000	2.289462

Cartesian coordinates of the B3LYP/6-31G** optimized geometries of the (C_1,C_4) compound in the lowest triplet state

C	0.675323	0.000000	-1.855117
C	0.660135	0.000000	-0.415823
C	1.893886	0.000000	0.310274
C	3.114332	0.000000	-0.404315
C	3.047300	0.000000	-1.777762
C	1.906871	0.000000	-2.546517
H	1.923165	0.000000	-3.631855
H	4.059443	0.000000	0.132032
C	1.850070	0.000000	1.747715
C	0.663062	0.000000	2.417236
C	-0.593963	0.000000	1.718320
C	-0.585708	0.000000	0.288363
C	-1.829032	0.000000	-0.421243
C	-1.799778	0.000000	-1.870478
C	-0.600671	0.000000	-2.477126
H	-2.736679	0.000000	-2.422159
C	-3.034052	0.000000	0.299931
C	-3.028549	0.000000	1.695539
C	-1.824380	0.000000	2.398413
H	-1.827955	0.000000	3.485061
H	-3.969771	0.000000	2.237452
H	-3.975833	0.000000	-0.241949
H	0.648544	0.000000	3.503987
H	2.790006	0.000000	2.292979

Cartesian coordinates of the B3LYP/6-31G** optimized geometries of the (C_1,C_5) compound in the lowest triplet state

C	0.643503	0.000000	-1.843663
C	0.634061	0.000000	-0.409245
C	1.867216	0.000000	0.318934
C	3.091218	0.000000	-0.389836
C	3.023999	0.000000	-1.762753
C	1.879878	0.000000	-2.526989
H	1.904738	0.000000	-3.613265
H	4.034650	0.000000	0.149214
C	1.825855	0.000000	1.756788
C	0.642083	0.000000	2.431885
C	-0.616260	0.000000	1.735746
C	-0.605149	0.000000	0.306464
C	-1.856194	0.000000	-0.400897
C	-3.064499	0.000000	0.315604
C	-3.054386	0.000000	1.710599
C	-1.848510	0.000000	2.412429
H	-1.852946	0.000000	3.499161
H	-3.993914	0.000000	2.255116
H	-4.002012	0.000000	-0.231048
C	-1.750382	0.000000	-1.814980
C	-0.622547	0.000000	-2.547212
H	-0.628328	0.000000	-3.634236
H	0.631044	0.000000	3.518714
H	2.767448	0.000000	2.299098

Cartesian coordinates of the B3LYP/6-31G** optimized geometries of the (C_1,C_7) compound in the lowest triplet state

C	0.624216	0.000000	-1.816821
C	0.624808	0.000000	-0.384620
C	1.857533	0.000000	0.344048
C	3.078161	0.000000	-0.370225
C	3.005241	0.000000	-1.743343
C	1.859789	0.000000	-2.504431
H	1.880787	0.000000	-3.590886
H	4.024265	0.000000	0.164307
C	1.813943	0.000000	1.781327
C	0.627918	0.000000	2.453561
C	-0.630281	0.000000	1.756517
C	-0.614263	0.000000	0.325308
C	-1.852283	0.000000	-0.405022
C	-1.820305	0.000000	-1.842498
C	-0.634185	0.000000	-2.514175
H	-0.620768	0.000000	-3.600644
H	-2.763547	0.000000	-2.379499
C	-3.005276	0.000000	0.365031
C	-3.075552	0.000000	1.739128
C	-1.859904	0.000000	2.440087
H	-1.865038	0.000000	3.527441
H	-4.023243	0.000000	2.269482
H	0.616214	0.000000	3.540324
H	2.753970	0.000000	2.326238

Cartesian coordinates of the B3LYP/6-31G** optimized geometries of the (C_1,C_8) compound in the lowest triplet state

C	-0.308616	1.787796	-0.537882
C	-0.308616	0.355807	-0.537882
C	-0.923835	-0.366840	-1.610137
C	-1.530675	0.349341	-2.667788
C	-1.493891	1.722191	-2.603677
C	-0.922637	2.478861	-1.608048
H	-0.931139	3.565447	-1.622868
H	-2.001798	-0.184334	-3.488901
C	-0.906110	-1.803836	-1.579245
C	-0.317732	-2.482135	-0.553770
C	0.308610	-1.787921	0.537871
C	0.308643	-0.355922	0.537929
C	0.923828	0.366982	1.610125
C	0.906094	1.803845	1.579217
C	0.317687	2.482221	0.553691
H	0.313036	3.568896	0.545586
H	1.375240	2.344407	2.396884
C	1.530673	-0.349327	2.667785
C	1.493909	-1.722222	2.603709
C	0.922694	-2.478849	1.608148
H	0.931110	-3.565506	1.622816
H	2.001849	0.184115	3.488990
H	-0.313113	-3.568814	-0.545719
H	-1.375340	-2.344160	-2.397058

Cartesian coordinates of the B3LYP/6-31G** optimized geometries of the (C_2,C_4) compound in the lowest triplet state

C	0.646460	0.000000	-1.866092
C	0.632355	0.000000	-0.421066
C	1.871006	0.000000	0.292906
C	3.085411	0.000000	-0.418402
C	3.106049	0.000000	-1.821978
C	1.892312	0.000000	-2.471412
H	4.048390	0.000000	-2.361746
H	4.023123	0.000000	0.131969
C	1.824082	0.000000	1.731609
C	0.637592	0.000000	2.402599
C	-0.621562	0.000000	1.705822
C	-0.614241	0.000000	0.275914
C	-1.854049	0.000000	-0.441062
C	-1.821340	0.000000	-1.891622
C	-0.621458	0.000000	-2.498539
H	-2.758015	0.000000	-2.443405
C	-3.059973	0.000000	0.278602
C	-3.055498	0.000000	1.674610
C	-1.853833	0.000000	2.382405
H	-1.861439	0.000000	3.468996
H	-3.998100	0.000000	2.214277
H	-4.001453	0.000000	-0.263713
H	0.624409	0.000000	3.489249
H	2.763202	0.000000	2.278606

Cartesian coordinates of the B3LYP/6-31G** optimized geometries of the (C_2,C_5) compound in the lowest triplet state

C	0.614919	0.000000	-1.856957
C	0.606434	0.000000	-0.417500
C	1.843760	0.000000	0.302181
C	3.061224	0.000000	-0.401975
C	3.081498	0.000000	-1.804923
C	1.867590	0.000000	-2.452785
H	4.022818	0.000000	-2.346856
H	3.997310	0.000000	0.150920
C	1.798987	0.000000	1.741313
C	0.616346	0.000000	2.418275
C	-0.643577	0.000000	1.723261
C	-0.633228	0.000000	0.294213
C	-1.880341	0.000000	-0.419994
C	-3.089969	0.000000	0.294303
C	-3.081177	0.000000	1.689582
C	-1.877729	0.000000	2.396185
H	-1.886176	0.000000	3.482862
H	-4.022099	0.000000	2.231842
H	-4.026952	0.000000	-0.253117
C	-1.770627	0.000000	-1.834734
C	-0.645581	0.000000	-2.570308
H	-0.642486	0.000000	-3.656429
H	0.606420	0.000000	3.504994
H	2.739986	0.000000	2.284961

Cartesian coordinates of the B3LYP/6-31G** optimized geometries of the (C_2,C_7) compound in the lowest triplet state

C	0.596597	0.000000	-1.830366
C	0.597163	0.000000	-0.392649
C	1.834088	0.000000	0.326725
C	3.049115	0.000000	-0.381873
C	3.064155	0.000000	-1.785308
C	1.847368	0.000000	-2.427780
H	4.003806	0.000000	-2.330002
H	3.987446	0.000000	0.167436
C	1.787434	0.000000	1.765548
C	0.602621	0.000000	2.439204
C	-0.657476	0.000000	1.743350
C	-0.642922	0.000000	0.312314
C	-1.877260	0.000000	-0.423644
C	-1.842974	0.000000	-1.862790
C	-0.658229	0.000000	-2.536074
H	-0.637853	0.000000	-3.621149
H	-2.786255	0.000000	-2.399448
C	-3.031298	0.000000	0.343988
C	-3.102360	0.000000	1.717971
C	-1.888797	0.000000	2.423107
H	-1.897903	0.000000	3.510376
H	-4.051926	0.000000	2.245217
H	0.592228	0.000000	3.525825
H	2.727100	0.000000	2.311403

Cartesian coordinates of the B3LYP/6-31G** optimized geometries of the (C_2,C_8) compound in the lowest triplet state

C	0.595273	0.000000	-1.800624
C	0.592808	0.000000	-0.362838
C	1.832396	0.000000	0.352511
C	3.047173	0.000000	-0.357022
C	3.063250	0.000000	-1.760150
C	1.845354	0.000000	-2.400272
H	4.002589	0.000000	-2.305223
H	3.985386	0.000000	0.192531
C	1.791166	0.000000	1.790432
C	0.608642	0.000000	2.468587
C	-0.650431	0.000000	1.773821
C	-0.649090	0.000000	0.341623
C	-1.881376	0.000000	-0.388514
C	-1.840154	0.000000	-1.826599
C	-0.657899	0.000000	-2.505042
H	-0.639861	0.000000	-3.590349
H	-2.781742	0.000000	-2.368802
C	-3.102594	0.000000	0.324213
C	-3.031095	0.000000	1.697605
C	-1.886740	0.000000	2.460140
H	-1.909270	0.000000	3.546576
H	-4.048331	0.000000	-0.210896
H	0.598745	0.000000	3.555111
H	2.732387	0.000000	2.333832

Cartesian coordinates of the B3LYP/6-31G** optimized geometries of the (C_2,C_9) compound in the lowest triplet state

C	0.618486	0.000000	-1.788602
C	0.620698	0.000000	-0.351419
C	1.858884	0.000000	0.366245
C	3.072462	0.000000	-0.344223
C	3.085766	0.000000	-1.748017
C	1.868397	0.000000	-2.388881
H	4.024931	0.000000	-2.293547
H	4.011688	0.000000	0.203511
C	1.818061	0.000000	1.805992
C	0.638576	0.000000	2.488679
C	-0.618465	0.000000	1.788399
C	-0.620643	0.000000	0.351421
C	-1.858939	0.000000	-0.366364
C	-1.818060	0.000000	-1.805857
C	-0.638454	0.000000	-2.488554
H	-0.624019	0.000000	-3.573774
H	-2.760352	0.000000	-2.347181
C	-3.072498	0.000000	0.344367
C	-3.085937	0.000000	1.748128
C	-1.868323	0.000000	2.388625
H	-4.024933	0.000000	2.293924
H	-4.011743	0.000000	-0.203392
H	0.623805	0.000000	3.573851
H	2.760563	0.000000	2.346977

Cartesian coordinates of the B3LYP/6-31G** optimized geometries of the (C_2,C_{11}) compound in the lowest triplet state

C	0.644419	0.000000	-1.784521
C	0.646362	0.000000	-0.346826
C	1.891262	0.000000	0.362747
C	3.103210	0.000000	-0.348999
C	3.112032	0.000000	-1.752931
C	1.892443	0.000000	-2.388622
H	4.049331	0.000000	-2.301754
H	4.043202	0.000000	0.197184
C	1.852887	0.000000	1.813316
C	0.650572	0.000000	2.413353
C	-0.623686	0.000000	1.789290
C	-0.600154	0.000000	0.352705
C	-1.834209	0.000000	-0.368401
C	-1.792681	0.000000	-1.807331
C	-0.611386	0.000000	-2.486622
H	-0.593908	0.000000	-3.571860
H	-2.734621	0.000000	-2.349397
C	-3.043089	0.000000	0.348769
C	-3.050516	0.000000	1.744370
C	-1.855520	0.000000	2.464491
H	-1.863324	0.000000	3.549702
H	-3.997368	0.000000	2.276199
H	-3.981682	0.000000	-0.198897
H	2.786694	0.000000	2.370097

Cartesian coordinates of the B3LYP/6-31G** optimized geometries of the (C_2,C_{12}) compound in the lowest triplet state

C	0.678358	0.000000	-1.827486
C	0.681275	0.000000	-0.387328
C	1.916552	0.000000	0.351871
C	1.872931	0.000000	1.789446
C	0.682982	0.000000	2.453323
C	-0.571707	0.000000	1.749076
C	-0.560782	0.000000	0.318791
C	-1.795199	0.000000	-0.403568
C	-1.758299	0.000000	-1.841792
C	-0.579134	0.000000	-2.524825
H	-0.564685	0.000000	-3.610102
H	-2.701641	0.000000	-2.381232
C	-3.003923	0.000000	0.313862
C	-3.006296	0.000000	1.708861
C	-1.806387	0.000000	2.420505
H	-1.817655	0.000000	3.507165
H	-3.950423	0.000000	2.245697
H	-3.943271	0.000000	-0.232505
H	0.663639	0.000000	3.539849
H	2.813186	0.000000	2.331518
C	3.080681	0.000000	-0.406598
C	3.144870	0.000000	-1.787467
C	1.925759	0.000000	-2.439282
H	4.090761	0.000000	-2.324719

Cartesian coordinates of the B3LYP/6-31G** optimized geometries of the (C_2,C_{14}) compound in the lowest triplet state

C	0.678358	0.000000	-1.827486
C	0.681275	0.000000	-0.387328
C	1.916552	0.000000	0.351871
C	1.872931	0.000000	1.789446
C	0.682982	0.000000	2.453323
C	-0.571707	0.000000	1.749076
C	-0.560782	0.000000	0.318791
C	-1.795199	0.000000	-0.403568
C	-1.758299	0.000000	-1.841792
C	-0.579134	0.000000	-2.524825
H	-0.564685	0.000000	-3.610102
H	-2.701641	0.000000	-2.381232
C	-3.003923	0.000000	0.313862
C	-3.006296	0.000000	1.708861
C	-1.806387	0.000000	2.420505
H	-1.817655	0.000000	3.507165
H	-3.950423	0.000000	2.245697
H	-3.943271	0.000000	-0.232505
H	0.663639	0.000000	3.539849
H	2.813186	0.000000	2.331518
C	3.080681	0.000000	-0.406598
C	3.144870	0.000000	-1.787467
C	1.925759	0.000000	-2.439282
H	4.090761	0.000000	-2.324719

Cartesian coordinates of the B3LYP/6-31G** optimized geometries of the (C_4,C_5) compound in the lowest triplet state

C	0.578713	0.000000	-1.861305
C	0.579526	0.000000	-0.423863
C	1.826153	0.000000	0.274477
C	3.023717	0.000000	-0.460914
C	3.007449	0.000000	-1.856287
C	1.801475	0.000000	-2.556945
H	1.791906	0.000000	-3.642063
H	3.944420	0.000000	-2.405453
H	3.970764	0.000000	0.071832
C	1.806949	0.000000	1.713495
C	0.634430	0.000000	2.408053
C	-0.636759	0.000000	1.733578
C	-0.650040	0.000000	0.304244
C	-1.910134	0.000000	-0.386333
C	-3.107920	0.000000	0.351570
C	-3.073016	0.000000	1.745880
C	-1.856993	0.000000	2.430530
H	-1.844542	0.000000	3.517057
H	-4.004767	0.000000	2.303846
H	-4.054877	0.000000	-0.178265
C	-1.864406	0.000000	-1.810978
C	-0.692600	0.000000	-2.505675
H	0.640722	0.000000	3.494843
H	2.757110	0.000000	2.241048

Cartesian coordinates of the B3LYP/6-31G** optimized geometries of the (C_4,C_{11}) compound in the lowest triplet state

C	0.617491	0.000000	-1.796011
C	0.619860	0.000000	-0.358720
C	1.872868	0.000000	0.332782
C	3.066846	0.000000	-0.407439
C	3.044503	0.000000	-1.803080
C	1.834711	0.000000	-2.497138
H	1.819450	0.000000	-3.582239
H	3.980064	0.000000	-2.354618
H	4.016141	0.000000	0.121187
C	1.860375	0.000000	1.782493
C	0.666399	0.000000	2.399704
C	-0.617541	0.000000	1.795665
C	-0.619588	0.000000	0.358669
C	-1.873017	0.000000	-0.332600
C	-1.860264	0.000000	-1.782493
C	-0.666629	0.000000	-2.399983
H	-2.803314	0.000000	-2.323529
C	-3.066658	0.000000	0.407404
C	-3.044473	0.000000	1.803399
C	-1.834919	0.000000	2.497270
H	-1.819015	0.000000	3.582317
H	-3.980273	0.000000	2.354522
H	-4.016057	0.000000	-0.121012
H	2.803201	0.000000	2.323841

Cartesian coordinates of the B3LYP/6-31G** optimized geometries of the (C_4,C_{12}) compound in the lowest triplet state

C	0.638366	0.000000	-1.814366
C	0.638719	0.000000	-0.378115
C	1.897438	0.000000	0.312155
C	3.095591	0.000000	-0.422477
C	3.069246	0.000000	-1.817526
C	1.858254	0.000000	-2.511375
H	1.844859	0.000000	-3.596579
H	4.003402	0.000000	-2.371108
H	4.040465	0.000000	0.111345
C	1.809190	0.000000	1.728454
C	0.689794	0.000000	2.472501
C	-0.586226	0.000000	1.783500
C	-0.593393	0.000000	0.351419
C	-1.845700	0.000000	-0.343068
C	-1.836276	0.000000	-1.793457
C	-0.646082	0.000000	-2.417688
H	-2.781729	0.000000	-2.330170
C	-3.042023	0.000000	0.392834
C	-3.018586	0.000000	1.787844
C	-1.806870	0.000000	2.478906
H	-1.798161	0.000000	3.565340
H	-3.953244	0.000000	2.341201
H	-3.990628	0.000000	-0.136818
H	0.706384	0.000000	3.559540

Table S1. Total Energies (hartrees) of H_2, pyrene, and the C_1, C_2 and C_4 radicals. Benzene and o-benzyne are include for comparison. For the three radicals the expectation value of square of the total spin operator is given in parenthesis.

Compound	**B3LYP/6-31++G****
H_2	-1.178973
H•	-0.501666
Pyrene	-615.807985
C_1	-615.119484 (0.757)
C_2	-615.118843 (0.761)
C_4	-615.119471 (0.760)
Benzene	-232. 268451
o-Benzyne	-230.928491

Table S2. B3LYP/&-31++G** total Energies (hartrees) of the (C_1,C_2), (C_1,C_4), (C_1,C_5), (C_1,C_7), (C_1,C_8), (C_2,C_4), (C_2,C_5), (C_2,C_7), (C_2,C_8), (C_2,C_9), (C_2,C_{11}), (C_2,C_{12}), (C_2,C_{14}), (C_4,C_5), (C_4,C_{11}), and (C_4,C_{12}) compounds in the lowest triplet and singlet states. Notice that for the (C_1,C_2), (C_2,C_{14}), and (C_4,C_5) the singlet is closed shell whereas in the rest of pyrene dehydrogenated compounds it is an open shell singlet. The (C_1,C_2), (C_2,C_{14}), and (C_4,C_5) ground state is a closed shell because a benzyne-like species is formed. In the case of broken symmetry solutions, the singlet energies have been obtained from the broken symmetry (BS) and triplet (T) energies as $E_S=2E_{BS}-E_T$ (cf. refs. 29 and 36).The expectation value of square of the total spin operator is also reported.

Compound	**Triplet**	**$<S^2>$**	**Singlet**	**$<S^2>$**
(C_1,C_2)	-614.418771	2.009	-614.468446	0.000
(C_1,C_4)	-614.430435	2.013	-614.430731	1.016
(C_1,C_5)	-614.430279	2.022	-614.433021	0.987
(C_1,C_7)	-614.430252	2.023	-614.429732	1.014
(C_1,C_8)	-614.430602	2.011	-614.430648	1.018
(C_2,C_4)	-614.429035	2.030	-614.429647	0.990
(C_2,C_5)	-614.429597	2.012	-614.431119	1.017
(C_2,C_7)	-614.429297	2.014	-614.429647	1.029
(C_2,C_8)	-614.430239	2.023	-614.429767	1.014
(C_2,C_9)	-614.429175	2.014	-614.430599	1.022
(C_2,C_{11})	-614.429763	2.012	-614.430573	1.026
(C_2,C_{12})	-614.43034	2.028	-614.42938	1.014
(C_2,C_{14})	-614.425752	2.034	-614.440859	0.000
(C_4,C_5)	-614.416666	2.005	-614.473792	0.000
(C_4,C_{11})	-614.430529	2.016	-614.431243	1.019
(C_4,C_{12})	-614.430119	2.024	-614.433171	0.988

Table S3. CASSCF/CASPT2 total Energies (hartrees) of the (C_1,C_2), (C_1,C_8), (C_2,C_{14}), and (C_4,C_5) compounds in the lowest triplet and singlet states and at the B3LYP corresponding optimized geometries. These calculations are based on a CAS containing 2 active electrons and 2 active orbitals. The ANO (3s,2p,1d) and (2s,1p) is used for C and H, respectively.

Compound	Triplet	Singlet
	CASSCF	
(C_1,C_2)	-610.4725003	-610.545556
(C_1,C_8)	-610.5399963	-610.539963
(C_2,C_{14})	-610.4596566	-610.505497
(C_4,C_5)	-610.4913954	-610.560528
	CASPT2	
(C_1,C_2)	-611.666797	-611.752074
(C_1,C_8)	-611.705229	-611.705366
(C_2,C_{14})	-611.652102	-611.733904
(C_4,C_5)	-611.673545	-611.760306

Table S4. CASSCF/CASPT2 total Energies (hartrees) of the (C_1,C_2), (C_1,C_8), (C_2,C_{14}), and (C_4,C_5) compounds in the lowest triplet and singlet states and at the B3LYP corresponding optimized geometries. These calculations are based on a CAS containing 4 active electrons and 4 active orbitals. The ANO (3s,2p,1d) and (2s,1p) is used for C and H, respectively.

Compound	Triplet	Singlet
	CASSCF	
(C_1,C_2)	-610.4963088	-610.5490651
(C_1,C_8)	-610.5551254	-610.5551651
(C_2,C_{14})	-610.5525396	-610.5312983
(C_4,C_5)	-610.5306726	-610.562759
	CASPT2	
(C_1,C_2)	-611.6635455	-611.7501246
(C_1,C_8)	-611.7055541	-611.7058392
(C_2,C_{14})	-611.7107931	-611.7348842
(C_4,C_5)	-611.7049885	-611.7560838