Supplementary Material (ESI) for PCCP

ELECTRONIC SUPPLEMENTARY INFORMATION

A Theoretical Study on the Thermal Ring Opening Rearrangement of 1*H*-bicyclo[3.1.0]hexa-3,5-dien-2-one: A Case of Two State Reactivity.

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1. Some Computational Details.

In order to reduce a systematic error found in the CASPT2 calculation that leads to a relative overestimation of the correlation energy for open shell systems, the H_0 Hamiltonian used in this work has been modified using the IPEA shift.[1] The value employed was the one recommended in ref. 1 (0.25 au). Though the use of the IPEA corrected H_0 Hamiltonian seems also to contribute to reduce the problem of the intruder states, in all the single point calculations carried out at each of the MEP points, an imaginary level shift[2] of 0.05 au was used to minimize the effects of some intruder states present at the initial steps of the MEP. All the single point CASPT2 computations along the MEP were carried out using two roots equal weights state average CASSCF wavefunctions as references for both the singlet and triplet states.

Table S1. CASSCF(8,8)/ANO-S [4s3p1d/2s1p] (left) and CASPT2/ANO-S [4s3p1d/2s1p] (right) optimised geometries for the most significant structures belonging to the singlet manifolds involved in the reaction. Coordinates in Bohrs

C 1.864483 -0.182050 0.029909	C 1.911601 -0.170808 0.027364
C 0.860922 2.486085 0.100988	C 0.889366 2.505693 0.048060
C -1.669910 2.575648 -0.190544	C -1.667259 2.575354 -0.195088
C -2.577979 -0.064590 -0.339633	C -2.541032 -0.066737 -0.296391
C -0.352902 -1.903299 -0.575956	C -0.338510 -1.895405 -0.532684
C -2.569649 -2.039872 1.165612	C -2.640588 -2.075599 1.187302
O 4.052502 -0.746439 0.232641	O 4.137962 -0.735587 0.199428
H 2.068449 4.065763 0.493400	H 2.092642 4.109857 0.454363
H -2.843728 4.221297 -0.087184	H -2.868168 4.224086 -0.063107
H -3.214433 -2.823709 2.908246	H -3.359738 -2.904976 2.903126
H -0.137900 -3.159897 -2.159778	H -0.136421 -3.136942 -2.154671
R(^{1}A)	**R(^{1}A)**
C -1.808847 -0.367520 -0.140751	C -1.842338 -0.337329 -0.108136
C -1.033774 2.336600 -0.219294	C -1.055143 2.363402 -0.211201
C 1.447684 2.656083 0.231812	C 1.454944 2.663531 0.201603
C 2.905020 0.302746 0.367983	C 2.908835 0.336265 0.409572
C 0.368979 -2.048542 0.548356	C 0.349937 -2.056754 0.410324
C 2.818702 -1.964244 -0.664560	C 2.895642 -1.948497 -0.628824
O -3.957036 -1.082940 -0.349815	O -4.043935 -1.056687 -0.113200
H -2.351133 3.809923 -0.674479	H -2.372090 3.855180 -0.694959
H 2.399266 4.445847 0.223684	H 2.434186 4.460852 0.128766
H 4.092446 -3.313562 -1.462109	H 4.241279 -3.327915 -1.300438
H 0.122981 -3.070560 2.292063	H 0.032971 -3.248218 2.059382
TS1(^{1}A)	**TS1(^{1}A)**
C 0.000000 0.000000 -3.638333	C 0.000000 0.000000 -3.658539
C 0.000000 2.337204 -2.105503	C 0.000000 2.337013 -2.122789
C 0.000000 2.381287 0.445510	C 0.000000 2.393077 0.447884
C 0.000000 0.000000 1.902904	C 0.000000 0.000000 1.904422
O 0.000000 0.000000 4.191167	O 0.000000 0.000000 4.233162
H 0.000000 4.094030 -3.128444	H 0.000000 4.115143 -3.150310
H 0.000000 4.104808 1.521142	H 0.000000 4.126834 1.546265
C 0.000000 -2.337204 -2.105503	C 0.000000 -2.337013 -2.122789
C 0.000000 -2.381287 0.445510	C 0.000000 -2.393077 0.447884
H 0.000000 -4.094030 -3.128444	H 0.000000 -4.115143 -3.150310
H 0.000000 -4.104808 1.521142	H 0.000000 -4.126834 1.546265
TS2(^{1}A$_1$)	**TS2(^{1}A$_1$)**
C 0.000000 0.000000 -3.369982	C 0.000000 0.000000 -3.360724
C 0.000000 2.329846 -2.189103	C 0.000000 2.349587 -2.200385
C 0.000000 2.334305 0.448790	C 0.000000 2.349050 0.444794
C 0.000000 0.000000 1.819117	C 0.000000 0.000000 1.842523
O 0.000000 0.000000 4.204346	O 0.000000 0.000000 4.241528
H 0.000000 4.059683 -3.246772	H 0.000000 4.092936 -3.273294
H 0.000000 4.062509 1.511314	H 0.000000 4.091452 1.524721
C 0.000000 -2.329846 -2.189103	C 0.000000 -2.349587 -2.200385
C 0.000000 -2.334305 0.448790	C 0.000000 -2.349050 0.444794
H 0.000000 -4.059683 -3.246772	H 0.000000 -4.092936 -3.273294
H 0.000000 -4.062509 1.511314	H 0.000000 -4.091452 1.524721
P(^{1}B$_1$)	**P(^{1}B$_1$)**
C 0.759721 0.000000 -3.325723	C 0.662118 0.000000 -3.297231
C 0.157369 2.321214 -2.169620	C 0.154312 2.339519 -2.198357
C 0.006152 2.360617 0.428202	C 0.013355 2.355111 0.433284
C 0.003427 0.000000 1.852009	C -0.016427 0.000000 1.847375
O -0.047511 0.000000 4.172925	O -0.095079 0.000000 4.228710
H 0.141399 4.040439 -3.247877	H 0.178754 4.076454 -3.283202
H -0.001337 4.089794 1.490661	H 0.039676 4.100182 1.509819
C 0.157369 -2.321214 -2.169620	C 0.154312 -2.339519 -2.198357
C 0.006152 -2.360617 0.428202	C 0.013355 -2.355111 0.433284
H 0.141399 -4.040439 -3.247877	H 0.178754 -4.076454 -3.283202
H -0.001337 -4.089794 1.490661	H 0.039676 -4.100182 1.509819
P(^{1}A')	**P(^{1}A')**

Table S2. CASSCF(8,8)/ANO-S [4s3p1d/2s1p] (left) and CASPT2/ANO-S [4s3p1d/2s1p] (right) optimised geometries for the most significant structures belonging to the triplet PES involved in the reaction. Coordinates in Bohrs

C -1.786685 -0.334293 0.016254 C -0.994337 2.337865 -0.332383 C 1.462668 2.609658 0.272391 C 2.583418 0.178888 1.086554 C 0.495978 -1.816243 0.877733 C 2.836190 -1.877046 -0.732491 O -3.877411 -1.172419 -0.250282 H -2.234617 3.756526 -1.075815 H 2.554340 4.305118 0.073603 H 4.157527 -3.413762 -0.642210 H 0.196509 -3.374472 2.144122 **R(^{3}A)**	C -1.822040 -0.304412 0.027976 C -1.035104 2.370345 -0.301411 C 1.463427 2.600199 0.251772 C 2.561291 0.182101 1.070274 C 0.496050 -1.798290 0.835361 C 2.948763 -1.859714 -0.719297 O -3.941750 -1.182346 -0.207955 H -2.286932 3.816937 -1.021649 H 2.601455 4.279737 -0.010679 H 4.214015 -3.460223 -0.502741 H 0.194404 -3.444513 2.015825 **R(^{3}A)**
C -1.751523 -0.282457 0.038568 C -1.005420 2.384985 -0.267574 C 1.496076 2.760839 0.107288 C 2.945647 0.484406 0.500652 C 0.420889 -2.078834 0.449138 C 2.694233 -1.878268 -0.946411 O -3.900891 -1.035766 0.059997 H -2.372142 3.808215 -0.724472 H 2.395069 4.579219 0.076639 H 4.080670 -3.352491 -0.768848 H 0.001676 -3.686020 1.627912 **TS1(^{3}A)**	C -1.788849 -0.245854 -0.037094 C -1.092131 2.412598 -0.156901 C 1.505205 2.721502 0.126869 C 2.871259 0.468236 0.235240 C 0.457281 -2.005471 0.397201 C 2.756921 -1.983959 -0.991734 O -3.929750 -1.142266 -0.145989 H -2.445693 3.896565 -0.535765 H 2.458428 4.534298 0.106223 H 4.126035 -3.466390 -0.628616 H 0.085579 -3.485430 1.783458 **TS1(^{3}A)**
C 0.000000 0.000000 -3.398873 C 0.000000 2.353326 -2.159369 C 0.000000 2.368071 0.432387 C 0.000000 0.000000 1.856783 O 0.000000 0.000000 4.172401 H 0.000000 4.080329 -3.224118 H 0.000000 4.092903 1.501056 C 0.000000 -2.353326 -2.159369 C 0.000000 -2.368071 0.432387 H 0.000000 -4.080329 -3.224118 H 0.000000 -4.092903 1.501056 **P(^{3}B$_1$)**	C 0.000000 0.000000 -3.380897 C 0.000000 2.359891 -2.182430 C 0.000000 2.365970 0.435040 C 0.000000 0.000000 1.856929 O 0.000000 0.000000 4.225745 H 0.000000 4.103443 -3.256477 H 0.000000 4.106423 1.518089 C 0.000000 -2.359891 -2.182430 C 0.000000 -2.365970 0.435040 H 0.000000 -4.103443 -3.256477 H 0.000000 -4.106423 1.518089 **P(^{3}B$_1$)**

Table S3. CASSCF(8,8)/ANO-S [4s3p1d/2s1p] (left) and CASPT2/ANO-S [4s3p1d/2s1p] (right) optimised geometries of the different minimum energy crossing points located. Coordinates in Bohrs.

C 0.000000 0.000000 -3.53962 C 0.000000 2.335460 -2.14878 C 0.000000 2.369381 0.43133 C 0.000000 0.000000 1.86512 O 0.000000 0.000000 4.17552 H 0.000000 4.083204 -3.18407 H 0.000000 4.094607 1.50188 C 0.000000 -2.335460 -2.14878 C 0.000000 -2.369381 0.43133 H 0.000000 -4.083204 -3.18407 H 0.000000 -4.094607 1.50188 **CI**	C 0.000000 0.000000 -3.676958 C 0.000000 2.336769 -2.143207 C 0.000000 2.392514 0.427681 C 0.000000 0.000000 1.882873 O 0.000000 0.000000 4.212115 H 0.000000 4.114903 -3.170468 H 0.000000 4.124980 1.527949 C 0.000000 -2.336769 -2.143207 C 0.000000 -2.392514 0.427681 H 0.000000 -4.114903 -3.170468 H 0.000000 -4.124980 1.527949 **CI**
C 0.973593 0.000000 -3.287566 C 0.122673 2.299481 -2.160408 C -0.026240 2.365461 0.418744 C 0.017216 0.000000 1.867367 O 0.023593 0.000000 4.169884 H 0.089481 4.009489 -3.255328 H -0.031712 4.100102 1.473120 C 0.122673 -2.299481 -2.160408 C -0.026240 -2.365461 0.418744 H 0.089481 -4.009489 -3.255328 H -0.031712 4.100102 1.473120 **ISC**	C 0.973593 0.000000 -3.287566 C 0.122673 2.299481 -2.160408 C -0.026240 2.365461 0.418744 C 0.017216 0.000000 1.867367 O 0.023593 0.000000 4.169884 H 0.089481 4.009489 -3.255328 H -0.031712 4.100102 1.473120 C 0.122673 -2.299481 -2.160408 C -0.026240 -2.365461 0.418744 H 0.089481 -4.009489 -3.255328 H -0.031712 4.100102 1.473120 **ISC**

Table S4. B3LYP/6-311+G(2df,2p) (left) and M05-2X/6-311+G(2df,2p) (right) optimised geometries for the most significant structures belonging to the singlet manifold involved in the reaction. Coordinates in Angstroms

C -0.978947 -0.191201 -0.024882	C -0.970444 -0.192394 -0.018451
C -0.556061 1.258646 -0.089469	C -0.549549 1.259401 -0.095544
C 0.767412 1.416775 0.089974	C 0.765711 1.417148 0.090107
C 1.343309 0.085556 0.249823	C 1.337256 0.077820 0.245909
C 0.277228 -0.971283 0.370638	C 0.277404 -0.969013 0.385671
O -2.112760 -0.593367 -0.120763	O -2.098721 -0.587658 -0.120170
C 1.576941 -1.018878 -0.390905	C 1.557266 -1.021883 -0.397433
H -1.244274 2.033910 -0.392019	H -1.239703 2.029783 -0.393091
H 1.329467 2.332178 -0.021774	H 1.326575 2.330011 -0.008076
H 2.124284 -1.527986 -1.166525	H 2.079601 -1.527096 -1.187296
H 0.158714 -1.558321 1.276919	H 0.160650 -1.542482 1.295212
R(^{1}A)	**R(^{1}A)**
C -0.984439 -0.119146 -0.046198	C -0.978116 -0.145768 -0.043340
C -0.549894 1.295887 -0.068862	C -0.544116 1.261600 -0.070933
C 0.780071 1.427901 0.078856	C 0.781806 1.391834 0.067969
C 1.488328 0.191571 0.225274	C 1.508175 0.173064 0.241523
C 0.184695 -1.031822 0.178109	C 0.164656 -1.085004 0.132318
O -2.138567 -0.501359 -0.040800	O -2.130470 -0.519680 -0.020423
C 1.541331 -1.001695 -0.304973	C 1.530235 -1.025246 -0.282123
H -1.240269 2.098442 -0.286877	H -1.237778 2.062173 -0.266347
H 1.326730 2.354252 -0.037288	H 1.324845 2.315606 -0.051809
H 2.261121 -1.752842 -0.596255	H 2.251711 -1.793297 -0.501723
H -0.021825 -1.737871 0.979599	H -0.076441 -1.854810 0.856302
TS1(^{1}A)	**TS1(^{1}A)**
C 0.000000 0.000000 1.003101	C 0.000000 0.000000 0.997046
O 0.000000 0.000000 2.220049	O 0.000000 0.000000 2.205283
C 0.000000 1.265864 0.230031	C 0.000000 1.265554 0.227410
C 0.000000 -1.265864 0.230031	C 0.000000 -1.265554 0.227410
C 0.000000 1.233266 -1.114798	C 0.000000 1.235042 -1.109539
C 0.000000 -1.233266 -1.114798	C 0.000000 -1.235042 -1.109539
C 0.000000 0.000000 -1.909350	C 0.000000 0.000000 -1.901909
H 0.000000 2.179133 0.813642	H 0.000000 2.173501 0.812645
H 0.000000 -2.179133 0.813642	H 0.000000 -2.173501 0.812645
H 0.000000 2.169703 -1.662177	H 0.000000 2.166270 -1.657127
H 0.000000 -2.169703 -1.662177	H 0.000000 -2.166270 -1.657127
TS2(^{1}A$_1$)	**TS2(^{1}A$_1$)**
C 0.000000 0.000000 0.000000	C 0.000000 0.000000 -0.004463
O 0.000000 0.000000 1.263170	O 0.000000 0.000000 1.246098
C 1.243093 0.000000 -0.748362	C 1.236952 0.000000 -0.744361
C -1.243093 0.000000 -0.748362	C -1.236952 0.000000 -0.744361
C 1.241131 0.000000 -2.136408	C 1.236325 0.000000 -2.121618
C -1.241131 0.000000 -2.136408	C -1.236325 0.000000 -2.121618
C 0.000000 0.000000 -2.755943	C 0.000000 0.000000 -2.728454
H 2.167182 0.000000 -0.177123	H 2.151370 0.000000 -0.172774
H -2.167182 0.000000 -0.177123	H -2.151370 0.000000 -0.172774
H 2.167156 0.000000 -2.704997	H 2.153276 0.000000 -2.688517
H -2.167156 0.000000 -2.704997	H -2.153276 0.000000 -2.688517
P(^{1}B$_1$)	**P(^{1}B$_1$)**
C 0.000141 -0.000491 0.000068	C 0.006285 -0.005847 0.003683
C 0.000062 -0.000356 1.469622	C 0.002793 0.005874 1.474553
C 1.175246 -0.000092 2.168614	C 1.168899 -0.005495 2.166520
C 2.294279 -0.333382 1.402958	C 2.280184 -0.382082 1.398728
C 1.312183 0.080702 -0.656849	C 1.320045 0.082095 -0.651989
O -1.045415 -0.023932 -0.645977	O -1.027897 -0.040003 -0.638148
C 2.464015 0.079523 0.079990	C 2.459360 0.069175 0.083228
H -0.960758 -0.072160 1.962620	H -0.959598 -0.030586 1.960366
H 1.202413 0.020258 3.250857	H 1.201475 0.023672 3.244757
H 3.441797 0.158598 -0.378368	H 3.437434 0.153052 -0.364927
H 1.323315 0.068941 -1.739030	H 1.326628 0.101703 -1.730466
P(^{1}A')	**P(^{1}A')**

Table S5. B3LYP/6-311+G(2df,2p) (left) and M05-2X/6-311+G(2df,2p) (right) optimised geometries for the most significant structures belonging to the triplet manifold involved in the reaction. Coordinates in Angstroms

C -0.976913 -0.092002 -0.001772 C -0.583529 1.278233 -0.049796 C 0.805311 1.410741 0.088225 C 1.439005 0.189858 0.110211 C 0.237827 -1.011417 0.323270 O -2.077613 -0.611481 -0.121488 C 1.463692 -1.103704 -0.385169 H -1.268746 2.086552 -0.253205 H 1.342243 2.346739 0.039066 H 2.192318 -1.896698 -0.341921 H 0.032491 -1.682598 1.157147 **R(^{3}A)**	C 0.965304 -0.075227 -0.022676 C 0.396746 1.290759 0.133955 C -0.930197 1.264434 -0.101771 C -1.365957 -0.073008 -0.463766 C -0.201331 -0.972074 -0.387884 O 2.119866 -0.391963 0.077470 C -1.358880 -1.117312 0.562251 H 0.992612 2.134145 0.437706 H -1.608539 2.087826 0.047840 H -1.378455 -1.067266 1.639714 H -0.015692 -1.807955 -1.047330 **R(^{3}A)**
C -0.976913 -0.092002 -0.001772 C -0.583529 1.278233 -0.049796 C 0.805311 1.410741 0.088225 C 1.439005 0.189858 0.110211 C 0.237827 -1.011417 0.323270 O -2.077613 -0.611481 -0.121488 C 1.463692 -1.103704 -0.385169 H -1.268746 2.086552 -0.253205 H 1.342243 2.346739 0.039066 H 2.192318 -1.896698 -0.341921 H 0.032491 -1.682598 1.157147 **TS1(^{3}A)**	C -0.970623 -0.098671 -0.003702 C -0.581928 1.275564 -0.050533 C 0.799884 1.412893 0.090344 C 1.428751 0.193487 0.106539 C 0.236336 -1.012617 0.312252 O -2.069311 -0.607149 -0.114502 C 1.463727 -1.099756 -0.386961 H -1.273418 2.075583 -0.244365 H 1.337597 2.344306 0.043392 H 2.187601 -1.888916 -0.305792 H 0.029414 -1.697988 1.128754 **TS1(^{3}A)**
C 0.000000 0.000000 0.000000 O 0.000000 0.000000 1.249360 C 1.243643 0.000000 -0.750851 C -1.243643 0.000000 -0.750851 C 1.238923 0.000000 -2.127404 C -1.238923 0.000000 -2.127404 C 0.000000 0.000000 -2.748589 H 2.164073 0.000000 -0.182518 H -2.164073 0.000000 -0.182518 H 2.159578 0.000000 -2.695874 H -2.159578 0.000000 -2.695874 **P(^{3}B$_1$)**	C 0.000000 0.000000 0.000000 O 0.000000 0.000000 1.241041 C 1.242392 0.000000 -0.746406 C -1.242392 0.000000 -0.746406 C 1.239776 0.000000 -2.117098 C -1.239776 0.000000 -2.117098 C 0.000000 0.000000 -2.733920 H 2.156087 0.000000 -0.174064 H -2.156087 0.000000 -0.174064 H 2.156706 0.000000 -2.684278 H -2.156706 0.000000 -2.684278 **P(^{3}B$_1$)**

Table S6. B3LYP/6-311+G(2df,2p) (left) and M05-2X/6-311+G(2df,2p) (right) optimised geometries of the different minimum energy crossing points located. Coordinates in Angstroms

C -1.711852 0.000084 0.279862	C -1.695909 -0.000011 0.318513
C -1.156486 1.226297 -0.093079	C -1.148681 1.224032 -0.095276
C 0.209112 1.249054 -0.052078	C 0.205435 1.251820 -0.052409
C 0.980149 0.000074 0.010314	C 0.976902 0.000012 0.021687
C 0.209203 -1.249105 -0.052213	C 0.205435 -1.251845 -0.052411
C -1.156667 -1.226515 -0.093234	C -1.148680 -1.224009 -0.095272
H -1.745358 2.132607 -0.164141	H -1.745106 2.119697 -0.177212
H 0.767335 2.173978 0.006514	H 0.764484 2.173449 -0.014967
H 0.767266 -2.173846 0.006526	H 0.764479 -2.173439 -0.014969
H -1.745328 -2.132638 -0.164255	H -1.745112 -2.119704 -0.177212
O 2.207168 0.000009 0.066169	O 2.191294 -0.000001 0.089919
ISC	**ISC**

Table S7. Absolute electronic energies (in au) and zero point corrected values (evaluated at the CASSCF level) for all the structures located on the PESs as computed at the CASSCF/ANO-S [4s3p1d/2s1p] and CASPT2//CASSCF/ANO-S [4s3p1d/2s1p] theoretical levels.

Surface	Structure	E			
		CASSCF	CASSCF+ZPE	CASPT2	CASPT2+ZPE
CSS	R(^{1}A)	-304.42272	-304.34096	-305.30391	-305.22216
	TS1(^{1}A)	-304.41308	-304.33241	-305.29305	-305.21238
	P(^{1}A')	-304.43830	-304.35766	-305.31168	-305.23104
OSS	TS2($^1A_1$)	-304.42958	-304.34786	-305.28630	-305.20458
	P($^1B_1$)	-304.43699	-304.35723	-305.31191	-305.23215
T	R(^{3}A)	-304.36323	-304.28170	-305.24393	-305.16240
	TS1(^{3}A)	-304.34100	-304.26175	-305.22188	-305.14263
	P($^3B_1$)	-304.46073	-304.37849	-305.32813	-305.24589
CSS-T	ISC	-304.43673	-	-[a]	-[a]
CSS-O	CI	-304.42589	-	-[a]	-[a]

[a] Differential correlation effects on the states involved break energetic degeneracy.

Table S8. Absolute electronic energies (in au) for all the structures located on the PESs as computed at the CASPT2/ANO-S [4s3p1d/2s1p] theoretical level.

Surface	Structure	E
CSS	R(^{1}A)	-305.30572
	TS1(^{1}A)	-305.29486
	P(^{1}A')	-305.31430
OSS	TS2($^1A_1$)	-305.28756
	P($^1B_1$)	-305.31281
T	R(^{3}A)	-305.24588
	TS1(^{3}A)	-305.22606
	P($^3B_1$)	-305.32979
CSS-T	ISC	-305.31359
CSS-O	CI	-305.28756

Table S9. B3LYP/6-311+G(2df,2p) optimized absolute electronic energies (a.u.), thermal corrections to Gibbs free energy (G, in a.u. and at 298,15 K) and zero point energy correction (E+ZPE, in au) for all stationary points on the three potential energy surfaces.

Surface	Structure	E	G	E+ZPE
CSS	R(^{1}A)	-306.21053	-306.16196	-306.13293
	TS1(^{1}A)	-306.20181	-306.15441	-306.12551
	P(^{1}A')	-306.22025	-306.17149	-306.14246
OSS	TS2($^1A_1$)	-306.19716	-306.14813	-306.11966
	P($^1B_1$)	-306.23883	-306.18902	-306.16082
T	R(^{3}A)	-306.15322	-306.10774	-306.07767
	TS1(^{3}A)	-306.14727	-306.10397	-306.07392
	P($^3B_1$)	-306.24540	-306.19608	-306.16690

Table S10. M05-2X/6-311+G(2df,2p) optimized absolute electronic energies (au), thermal corrections to Gibbs free energy (G, in a.u. and at 298,15 K) and zero point energy correction (E+ZPE, in au) for all stationary points on the three potential energy surfaces.

Surface	Structure	E	G	E+ZPE
CSS	R(^{1}A)	-306.17394	-306.12337	-306.09440
	TS1(^{1}A)	-306.15827	-306.10919	-306.08033
	P(^{1}A')	-306.17164	-306.12146	-306.09238
OSS	TS2($^1A_1$)	-306.15312	-306.10226	-306.07380
	P($^1B_1$)	-306.19310	-306.14178	-306.11363
T	R(^{3}A)	-306.11088	-306.06339	-306.03340
	TS1(^{3}A)	-306.10010	-306.05530	-306.02525
	P($^3B_1$)	-306.20241	-306.15153	-306.12238

Table S11. CCSD(T)/6-311+G(2df,2p) electronic energies (in au) calculated on CASPT2/ANO-S [4s3p1d/2s1p] optimized structures.

Structure	E
R(^{1}A)	-305.563629
P(^{1}A')	-305.563520

Table S12. B3LYP/6-311+G(2df,2p) lowest frequencies values (in cm^{-1}, at 298.15 K) and $\langle S^2 \rangle$ values for all the stationary points on the three potential energy surfaces.

Surface	Structure	Lowest Frequency	$\langle S^2 \rangle$
CSS	R(^{1}A)	171.4	0.0
	TS1(^{1}A)	-440.5 i	0.0
	P(^{1}A')	180.6	0.0
OSS	TS2($^1A_1$)	-3069.0 i	0.0
	P($^1B_1$)	199.5	1.02
T	R(^{3}A)	180.8	2.02
	TS1(^{3}A)	-706.2 i	2.00
	P($^3B_1$)	198,2	2.04

Table S13. M05-2X/6-311+G(2df,2p) lowest frequencies values (in cm^{-1}, at 298.15 K) and $\langle S^2 \rangle$ values for all the stationary points on the three potential energy surfaces.

Surface	Structure	Lowest Frequency	$\langle S^2 \rangle$
CSS	R(^{1}A)	169.7	0.0
	TS1(^{1}A)	-415.2 i	0.0
	P(^{1}A')	170.7	0.0
OSS	TS2($^1A_1$)	-945.1 i	0.0
	P($^1B_1$)	203.3	1.04
T	R(^{3}A)	176.8	2.02
	TS1(^{3}A)	-842.4 i	2.03
	P($^3B_1$)	198.4	2.06

References

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