# Supporting Information

**Towards a mechanistic understanding of the photochromism of dimethyldihydropyrenes**

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CASSCF(16,16)/cc-pVDZ optimized Cartesian coordinates in Å.

**DHP-GS**

| | | | |
|---|---|---|---|
| C | 2.8403016040 | -0.1235394301 | -1.2280667352 |
| C | 3.5241825623 | -0.1539913331 | 0.0000000000 |
| C | 2.8403016040 | -0.1235394301 | 1.2280667352 |
| C | 1.4488505982 | 0.0077149506 | 1.2785915898 |
| C | 1.4488505982 | 0.0077149506 | -1.2785915898 |
| C | 0.7005160231 | -0.0364704383 | 2.4697785200 |
| C | -0.7005160231 | 0.0364704383 | 2.4697785200 |
| C | -1.4488505982 | -0.0077149506 | 1.2785915898 |
| C | -2.8403016040 | 0.1235394301 | 1.2280667352 |
| C | -3.5241825623 | 0.1539913331 | 0.0000000000 |
| C | -2.8403016040 | 0.1235394301 | -1.2280667352 |
| C | -1.4488505982 | -0.0077149506 | -1.2785915898 |
| C | -0.7005160231 | 0.0364704383 | -2.4697785200 |
| C | 0.7005160231 | -0.0364704383 | -2.4697785200 |
| C | 0.6985006807 | 0.3622781293 | 0.0000000000 |
| C | -0.6985006807 | -0.3622781293 | 0.0000000000 |
| C | 0.5429408497 | 1.9104083076 | 0.0000000000 |
| C | -0.5429408497 | -1.9104083076 | 0.0000000000 |
| H | 3.3962384866 | -0.2524196296 | -2.1484119041 |
| H | 3.3962384866 | -0.2524196296 | 2.1484119041 |
| H | -3.3962384866 | 0.2524196296 | 2.1484119041 |
| H | -3.3962384866 | 0.2524196296 | -2.1484119041 |
| H | 4.5997912388 | -0.2708152390 | 0.0000000000 |
| H | -4.5997912388 | 0.2708152390 | 0.0000000000 |
| H | 1.2252490208 | -0.1084897373 | 3.4145025342 |
| H | -1.2252490208 | 0.1084897373 | 3.4145025342 |
| H | -1.2252490208 | 0.1084897373 | -3.4145025342 |
| H | 1.2252490208 | -0.1084897373 | -3.4145025342 |
| H | 0.0112393962 | 2.2596090105 | 0.8840530269 |
| H | 0.0112393962 | 2.2596090105 | -0.8840530269 |
| H | -0.0112393962 | -2.2596090105 | 0.8840530269 |
| H | -0.0112393962 | -2.2596090105 | -0.8840530269 |
| H | 1.5341515411 | 2.3655788918 | 0.0000000000 |
| H | -1.5341515411 | -2.3655788918 | 0.0000000000 |

**CPD-GS**

| | | | |
|---|---|---|---|
| C | 2.7416924612 | -0.1203400784 | -1.2023494101 |
| C | 3.4162239622 | -0.3437211901 | 0.0000000000 |
| C | 2.7416924612 | -0.1203400784 | 1.2023494101 |
| C | 1.4765612645 | 0.4908235931 | 1.2133474022 |
| C | 1.4765612645 | 0.4908235931 | -1.2133474022 |
| C | 0.6163392381 | 0.2878473106 | 2.4237952476 |
| C | -0.6163392381 | -0.2878473106 | 2.4237952476 |
| C | -1.4765612645 | -0.4908235931 | 1.2133474022 |
| C | -2.7416924612 | 0.1203400784 | 1.2023494101 |
| C | -3.4162239622 | 0.3437211901 | 0.0000000000 |
| C | -2.7416924612 | 0.1203400784 | -1.2023494101 |
| C | -1.4765612645 | -0.4908235931 | -1.2133474022 |
| C | -0.6163392381 | -0.2878473106 | -2.4237952476 |
| C | 0.6163392381 | 0.2878473106 | -2.4237952476 |
| C | 0.9517158846 | 0.9994183884 | 0.0000000000 |
| C | -0.9517158846 | -0.9994183884 | 0.0000000000 |
| C | -0.0932565994 | 2.0922476625 | 0.0000000000 |
| C | 0.0932565994 | -2.0922476625 | 0.0000000000 |
| H | 3.1707695460 | -0.4686791954 | -2.1336569852 |
| H | 3.1707695460 | -0.4686791954 | 2.1336569852 |
| H | -3.1707695460 | 0.4686791954 | 2.1336569852 |
| H | -3.1707695460 | 0.4686791954 | -2.1336569852 |
| H | 4.4012839473 | -0.7907475271 | 0.0000000000 |
| H | -4.4012839473 | 0.7907475271 | 0.0000000000 |
| H | 1.0858779220 | 0.4479590047 | 3.3887537749 |
| H | -1.0858779220 | -0.4479590047 | 3.3887537749 |
| H | -1.0858779220 | -0.4479590047 | -3.3887537749 |
| H | 1.0858779220 | 0.4479590047 | -3.3887537749 |
| H | -0.7239112995 | 2.0741445287 | 0.8829972842 |
| H | -0.7239112995 | 2.0741445287 | -0.8829972842 |
| H | 0.7239112995 | -2.0741445287 | 0.8829972842 |
| H | 0.7239112995 | -2.0741445287 | -0.8829972842 |
| H | 0.4374834790 | 3.0492597291 | 0.0000000000 |
| H | -0.4374834790 | -3.0492597291 | 0.0000000000 |

**DHP-LE**

| | | | |
|---|---|---|---|
| C | 2.8545987865 | -0.1182286583 | -1.2284138698 |
| C | 3.5467750151 | -0.1540636862 | 0.0000000000 |
| C | 2.8545987865 | -0.1182286583 | 1.2284138698 |
| C | 1.4540298727 | 0.0260017573 | 1.2742840478 |
| C | 1.4540298727 | 0.0260017573 | -1.2742840478 |
| C | 0.7049893367 | -0.0289343754 | 2.4712996499 |
| C | -0.7049893367 | 0.0289343754 | 2.4712996499 |
| C | -1.4540298727 | -0.0260017573 | 1.2742840478 |
| C | -2.8545987865 | 0.1182286583 | 1.2284138698 |
| C | -3.5467750151 | 0.1540636862 | 0.0000000000 |
| C | -2.8545987865 | 0.1182286583 | -1.2284138698 |
| C | -1.4540298727 | -0.0260017573 | -1.2742840478 |
| C | -0.7049893367 | 0.0289343754 | -2.4712996499 |
| C | 0.7049893367 | -0.0289343754 | -2.4712996499 |
| C | 0.6982701151 | 0.3769344746 | 0.0000000000 |
| C | -0.6982701151 | -0.3769344746 | 0.0000000000 |
| C | 0.4994878405 | 1.9169062184 | 0.0000000000 |
| C | -0.4994878405 | -1.9169062184 | 0.0000000000 |
| H | 3.4037463717 | -0.2466747577 | -2.1524839505 |
| H | 3.4037463717 | -0.2466747577 | 2.1524839505 |
| H | -3.4037463717 | 0.2466747577 | 2.1524839505 |
| H | -3.4037463717 | 0.2466747577 | -2.1524839505 |
| H | 4.6214131949 | -0.2742507946 | 0.0000000000 |
| H | -4.6214131949 | 0.2742507946 | 0.0000000000 |
| H | 1.2289156600 | -0.1106163196 | 3.4153458012 |
| H | -1.2289156600 | 0.1106163196 | 3.4153458012 |
| H | -1.2289156600 | 0.1106163196 | -3.4153458012 |
| H | 1.2289156600 | -0.1106163196 | -3.4153458012 |
| H | -0.0443799637 | 2.2490385795 | 0.8833959456 |
| H | -0.0443799637 | 2.2490385795 | -0.8833959456 |
| H | 0.0443799637 | -2.2490385795 | 0.8833959456 |
| H | 0.0443799637 | -2.2490385795 | -0.8833959456 |
| H | 1.4752026214 | 2.4052540649 | 0.0000000000 |
| H | -1.4752026214 | -2.4052540649 | 0.0000000000 |

**CPD-Z**

| | | | |
|---|---|---|---|
| C | 2.8209150394 | -0.2013245534 | -1.2155852494 |
| C | 3.5145769669 | -0.2943861861 | 0.0000000000 |
| C | 2.8209150394 | -0.2013245534 | 1.2155852494 |
| C | 1.4597708833 | 0.0871918179 | 1.2564214070 |
| C | 1.4597708833 | 0.0871918179 | -1.2564214070 |
| C | 0.6868144544 | 0.0311642652 | 2.4678642766 |
| C | -0.6868144544 | -0.0311642652 | 2.4678642766 |
| C | -1.4597708833 | -0.0871918179 | 1.2564214070 |
| C | -2.8209150394 | 0.2013245534 | 1.2155852494 |
| C | -3.5145769669 | 0.2943861861 | 0.0000000000 |
| C | -2.8209150394 | 0.2013245534 | -1.2155852494 |
| C | -1.4597708833 | -0.0871918179 | -1.2564214070 |
| C | -0.6868144544 | -0.0311642652 | -2.4678642766 |
| C | 0.6868144544 | 0.0311642652 | -2.4678642766 |
| C | 0.7502920441 | 0.4504573747 | 0.0000000000 |
| C | -0.7502920441 | -0.4504573747 | 0.0000000000 |
| C | 0.3525592498 | 1.9480645984 | 0.0000000000 |
| C | -0.3525592498 | -1.9480645984 | 0.0000000000 |
| H | 3.3463890287 | -0.3857160986 | -2.1445825107 |
| H | 3.3463890287 | -0.3857160986 | 2.1445825107 |
| H | -3.3463890287 | 0.3857160986 | 2.1445825107 |
| H | -3.3463890287 | 0.3857160986 | -2.1445825107 |
| H | 4.5735219312 | -0.5113179598 | 0.0000000000 |
| H | -4.5735219312 | 0.5113179598 | 0.0000000000 |
| H | 1.2169856598 | 0.0068218797 | 3.4117926995 |
| H | -1.2169856598 | -0.0068218797 | 3.4117926995 |
| H | -1.2169856598 | -0.0068218797 | -3.4117926995 |
| H | 1.2169856598 | 0.0068218797 | -3.4117926995 |
| H | -0.2255844853 | 2.2031737750 | 0.8852691106 |
| H | -0.2255844853 | 2.2031737750 | -0.8852691106 |
| H | 0.2255844853 | -2.2031737750 | 0.8852691106 |
| H | 0.2255844853 | -2.2031737750 | -0.8852691106 |
| H | 1.2652969304 | 2.5463106217 | 0.0000000000 |
| H | -1.2652969304 | -2.5463106217 | 0.0000000000 |

**CPD-B**

| | | | |
|---|---|---|---|
| C | 2.8532399354 | -0.0287121570 | -1.2208093409 |
| C | 3.5433777939 | -0.1165922632 | 0.0000000000 |
| C | 2.8532399354 | -0.0287121570 | 1.2208093409 |
| C | 1.4893111093 | 0.2779030381 | 1.2532602843 |
| C | 1.4893111093 | 0.2779030381 | -1.2532602843 |
| C | 0.6855589426 | 0.1122873224 | 2.4433345407 |
| C | -0.6855589426 | -0.1122873224 | 2.4433345407 |
| C | -1.4893111093 | -0.2779030381 | 1.2532602843 |
| C | -2.8532399354 | 0.0287121570 | 1.2208093409 |
| C | -3.5433777939 | 0.1165922632 | 0.0000000000 |
| C | -2.8532399354 | 0.0287121570 | -1.2208093409 |
| C | -1.4893111093 | -0.2779030381 | -1.2532602843 |
| C | -0.6855589426 | -0.1122873224 | -2.4433345407 |
| C | 0.6855589426 | 0.1122873224 | -2.4433345407 |
| C | 0.8380156049 | 0.6688411182 | 0.0000000000 |
| C | -0.8380156049 | -0.6688411182 | 0.0000000000 |
| C | 0.1338329351 | 2.0193106365 | 0.0000000000 |
| C | -0.1338329351 | -2.0193106365 | 0.0000000000 |
| H | 3.3714987493 | -0.2553042665 | -2.1444901905 |
| H | 3.3714987493 | -0.2553042665 | 2.1444901905 |
| H | -3.3714987493 | 0.2553042665 | 2.1444901905 |
| H | -3.3714987493 | 0.2553042665 | -2.1444901905 |
| H | 4.5968659651 | -0.3613742728 | 0.0000000000 |
| H | -4.5968659651 | 0.3613742728 | 0.0000000000 |
| H | 1.1971553322 | 0.1247041741 | 3.3984388897 |
| H | -1.1971553322 | -0.1247041741 | 3.3984388897 |
| H | -1.1971553322 | -0.1247041741 | -3.3984388897 |
| H | 1.1971553322 | 0.1247041741 | -3.3984388897 |
| H | -0.4832396329 | 2.1600520969 | 0.8841341797 |
| H | -0.4832396329 | 2.1600520969 | -0.8841341797 |
| H | 0.4832396329 | -2.1600520969 | 0.8841341797 |
| H | 0.4832396329 | -2.1600520969 | -0.8841341797 |
| H | 0.8990821923 | 2.8013954133 | 0.0000000000 |
| H | -0.8990821923 | -2.8013954133 | 0.0000000000 |

CASSCF(12,12)/cc-pVDZ optimized Cartesian coordinates in Å.

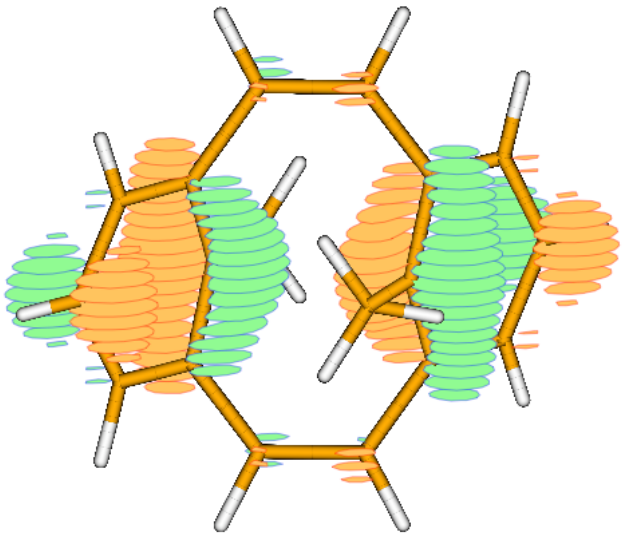
**CPD-CI**

| | | | |
|---|---|---|---|
| C | 2.5779531069 | 0.2426606152 | -1.1938251632 |
| C | 3.4223335231 | 0.3785844379 | -0.0326135345 |
| C | 2.8279389675 | 0.2292260509 | 1.1802449543 |
| C | 1.4023126673 | 0.1667435090 | 1.3231332425 |
| C | 1.2311974937 | 0.1495979796 | -1.1662607005 |
| C | 0.7363338723 | -0.2393040162 | 2.4641773052 |
| C | -0.6352791461 | -0.4689287873 | 2.4122213477 |
| C | -1.2664201082 | -0.2747949782 | 1.1411905681 |
| C | -2.5328176591 | 0.4928982094 | 1.1219301843 |
| C | -3.2597850285 | 0.6139056036 | 0.0097384347 |
| C | -2.7421000712 | 0.1758496527 | -1.2791357657 |
| C | -1.5871025630 | -0.5399509564 | -1.3080568033 |
| C | -0.7503829262 | -0.6027054550 | -2.5184696325 |
| C | 0.5359211933 | -0.2037976465 | -2.4112907571 |
| C | 0.5498814243 | 0.5178601638 | 0.1572528500 |
| C | -0.9747866060 | -1.0113950790 | -0.0677859326 |
| C | 0.0133607127 | 1.9446246575 | 0.1296742594 |
| C | -0.1671048370 | -2.2655278559 | -0.0023072970 |
| H | 3.0592234688 | 0.1430665935 | -2.1600991894 |
| H | 3.4194157282 | 0.1424690025 | 2.0839085169 |
| H | -2.8765085560 | 0.9043748273 | 2.0611509190 |
| H | -3.1832105847 | 0.5668173258 | -2.1860578161 |
| H | 4.4938573957 | 0.4384710393 | -0.1487905625 |
| H | -4.2086649723 | 1.1361158462 | 0.0422921695 |
| H | 1.2797888255 | -0.3624046149 | 3.3953452055 |
| H | -1.2383689113 | -0.3539465986 | 3.3027329847 |
| H | -1.1720624282 | -0.8626387819 | -3.4803967707 |
| H | 1.1564131483 | -0.1981077711 | -3.2987672527 |
| H | -0.3459446968 | 2.2601155689 | 1.1051574766 |
| H | -0.7589809272 | 2.0939925471 | -0.6227246815 |
| H | -0.4803526188 | -2.8434855430 | 0.8710915021 |
| H | 0.9061962663 | -2.0727772945 | 0.1200894747 |
| H | 0.8705447869 | 2.5646999953 | -0.1414644749 |
| H | -0.3027979102 | -2.8623072470 | -0.9032900507 |

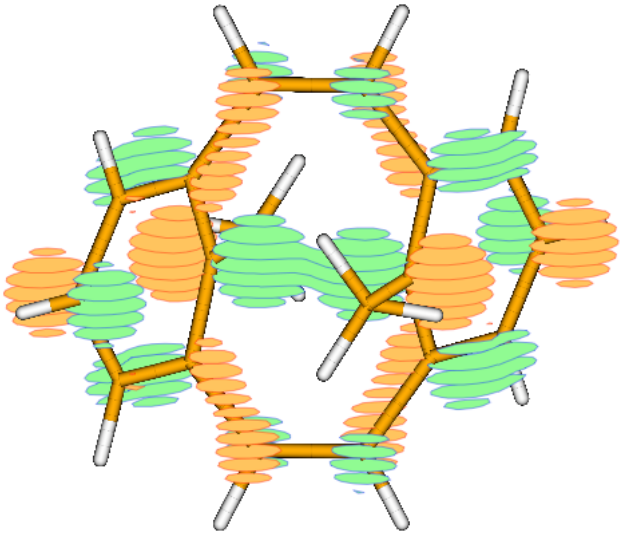
**DHP-CI**

| | | | |
|---|---|---|---|
| C | -2.7177915845 | -0.4241735431 | 1.2378430637 |
| C | -3.3522015062 | -0.6575090461 | 0.0000000000 |
| C | -2.7177915845 | -0.4241735431 | -1.2378430637 |
| C | -1.4294817523 | 0.0540393419 | -1.2791308122 |
| C | -1.4294817523 | 0.0540393419 | 1.2791308122 |
| C | -0.5678200951 | 0.4227813740 | -2.4147969650 |
| C | 0.7501614166 | 0.7263247979 | -2.2071311654 |
| C | 1.4739166991 | 0.2659565029 | -0.9668995080 |
| C | 2.8545856272 | -0.2635488954 | -1.1545178297 |
| C | 3.5789823541 | -0.5403863637 | 0.0000000000 |
| C | 2.8545856272 | -0.2635488954 | 1.1545178297 |
| C | 1.4739166991 | 0.2659565029 | 0.9668995080 |
| C | 0.7501614166 | 0.7263247979 | 2.2071311654 |
| C | -0.5678200951 | 0.4227813740 | 2.4147969650 |
| C | -0.7412270130 | 0.4040488580 | 0.0000000000 |
| C | 0.5971957887 | -0.4186964729 | 0.0000000000 |
| C | -0.6400133073 | 1.9907828779 | 0.0000000000 |
| C | 0.4038956269 | -1.9276131621 | 0.0000000000 |
| H | -3.2626042942 | -0.6282615317 | 2.1523878834 |
| H | -3.2626042942 | -0.6282615317 | -2.1523878834 |
| H | 3.2384007833 | -0.4405503556 | -2.1499524230 |
| H | 3.2384007833 | -0.4405503556 | 2.1499524230 |
| H | -4.3663908001 | -1.0332470711 | 0.0000000000 |
| H | 4.5743926054 | -0.9582219158 | 0.0000000000 |
| H | -1.0052465469 | 0.5789443738 | -3.3942303754 |
| H | 1.3377381856 | 1.1284444797 | -3.0236069953 |
| H | 1.3377381856 | 1.1284444797 | 3.0236069953 |
| H | -1.0052465469 | 0.5789443738 | 3.3942303754 |
| H | 0.3741742451 | 2.3785519012 | 0.0000000000 |
| H | -1.1492443178 | 2.3920316870 | 0.8729514897 |
| H | -0.1454584147 | -2.2592335241 | -0.8820657609 |
| H | 1.3710391940 | -2.4316189998 | 0.0000000000 |
| H | -1.1492443178 | 2.3920316870 | -0.8729514897 |
| H | -0.1454584147 | -2.2592335241 | 0.8820657609 |

**Figure S1.** Contour plots of the frontier molecular orbitals, HOMO and LUMO, of CPD-GS at CASSCF(16,16)/cc-pVDZ level. The symmetry of the two orbitals illustrates the forbidden character of the thermal ring-closure and the allowed character of the photochemical ring-closure according to the Woodward-Hoffman rule.



**HOMO**



**LUMO**

**Figure S2.** CASSCF(16,16)/cc-pVDZ optimized structures in $C_{2h}$ symmetry. $\phi$ is a dihedral angle measuring the planarity of the system. $q$ is the transannular distance.

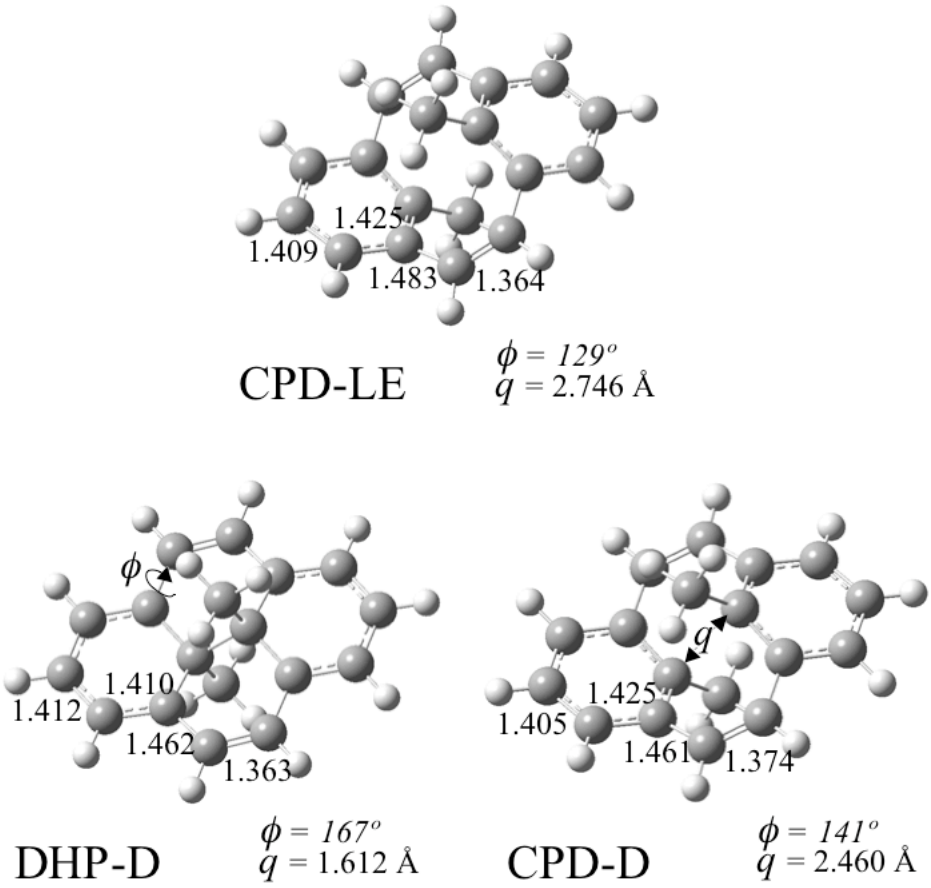


**Table S1.** CASSCF(16,16)/cc-pVDZ energies in Hartrees.

| Geometries[a] | GS energy | LE energy | Z energy | B energy | D energy |
|---|---|---|---|---|---|
| DHP-GS | -691.125964 | -691.060808 | -690.957879 | -690.983279 | -690.983563 |
| CPD-GS | -691.107833 | -690.944080 | -690.894478 | -690.889803 | -690.954235 |
| DHP-LE | -691.124924 | -691.061842 | | | |
| CPD-LE | | -690.950027 | | | |
| CPD-Z | -691.102457 | | -690.967385 | | |
| DHP-B | | | | -690.997126 | |
| CPD-B | | | | -690.994376 | |
| DHP-D | | | | | -690.996466 |
| CPD-D | | | | | -690.968876 |

[a] Geometries optimized at the CASSCF(16,16)/cc-pVDZ level of calculation.

**Table S2.** CASPT2(12,12)/cc-pVDZ energies[a] in Hartrees.

| Geometries[b] | GS energy | LE energy | Z energy | B energy | D energy |
|---|---|---|---|---|---|
| DHP-GS | -693.311817 | -693.243718 | -693.214500 | -693.171780 | -693.172306 |
| CPD-GS | -693.263712 | -693.118827 | -693.136528 | -693.076338 | -693.140334 |
| DHP-LE | -693.311346 | -693.245031 | | | |
| CPD-LE | | -693.127599 | | | |
| CPD-Z | -693.284815 | | -693.217797 | | |
| DHP-B | | | | -693.198612 | |
| CPD-B | *-693.235492* | | -693.199963 | -693.205831<br>*-693.208066* | |
| DHP-D | | | | | -693.179719 |
| CPD-D | | | | | -693.169162 |

[a] Values in italics have been computed using state-averaged orbitals.

[b] Geometries optimized at the CASSCF(16,16)/cc-pVDZ level of calculation.

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