# Electronic supporting information: On the Condensed Phase Ring-Closure of Vinylheptafulvalene and Ring-Opening of Gaseous Dihydroazulene

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## 1. Synthesis of the molecules

(i) DHA **7** (1.82 mg) was dissolved in cyclohexane (10 mL). A sample (0.200 mL) was diluted with cyclohexane (3.00 mL). A UV-Vis spectrum was acquired. The solution was irradiated with light (353 nm) for 90 s until no further change in the UV-Vis is observed. The cuvette was heated to 70 °C and the reaction was monitored by UV-Vis until the back-reaction was complete (16 h). DHA **7** was dissolved in deuterated cyclohexane (0.5 mL) using ultrasound and the solution was irradiated with light (353 nm) for 2 h. $^{1}$H NMR showed a full conversion to Z-VHF **8**. The solution was then heated at 70 °C until the back-reaction was complete (16 h). NMR showed a complete conversion to DHA **7** (no DHA **9**).

(ii) DHA **7** (2 mg) was dissolved in cyclohexane (10 mL) and the solution was irradiated with light (353 nm) for 2 h. The solution was then concentrated in vacuum and redissolved in deuterated MeCN (1 mL) at 0 °C. $^{1}$H NMR showed a full conversion to Z-VHF **8**. The solution was now divided into two NMR-tubes. Tube A was left overnight at room temperature and tube B was irradiated with light (353 nm) for 1 h and then heated at 70 °C for 1 h. $^{1}$H NMR showed that tube A now was a mixture of DHA **7** and DHA **8** in the ratio 11 : 13 together with Z-VHF and tube B was a mixture of DHA **7** and DHA **8** in the ratio 1 : 2 (which is the same as if one irradiated DHA **7** in MeCN and then left it overnight [1,2]).

## 2. Absorption spectra

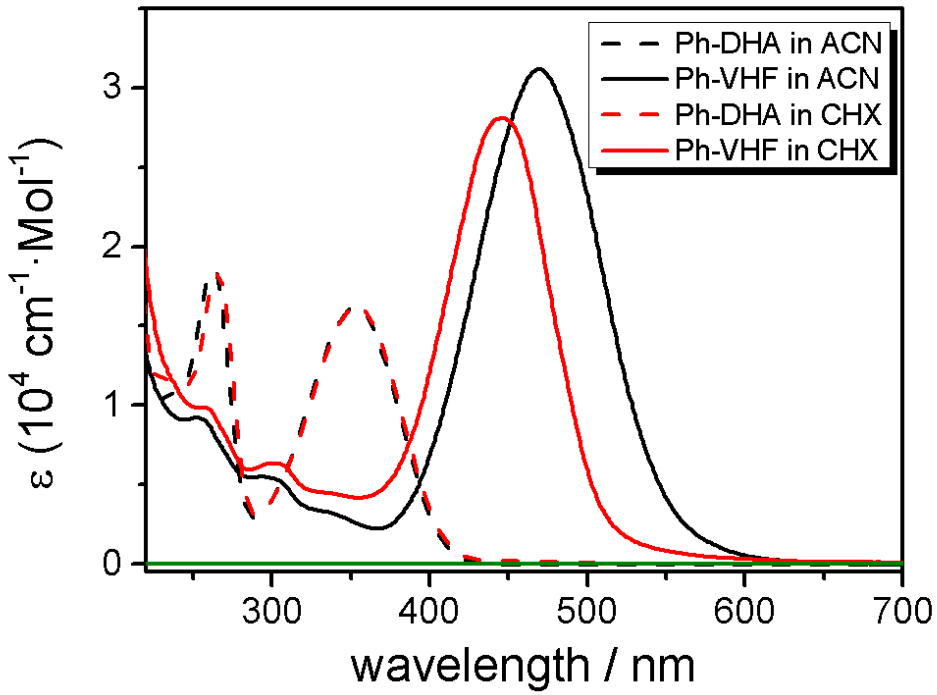


**Figure S1:** Absorption spectra of 2-phenyl-1,8a-dihydroazulene-1,1-dicarbonitrile (Ph-DHA) and its ring opened form (Ph-VHF) in acetonitrile (ACN) and cyclohexane (CHX).

**3. Decay associated spectrum of the TRPES measurement of Ph-DHA**

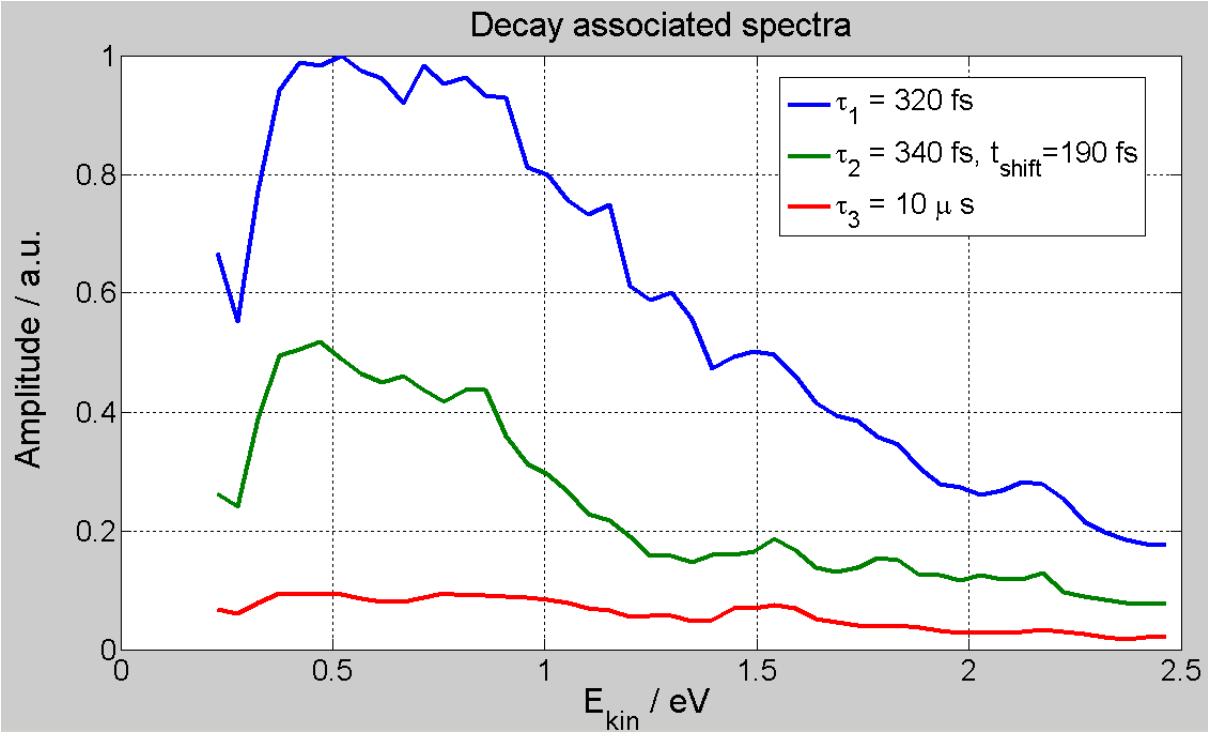


**Figure S2:** Decay associated spectra of Ph-DHA after excitation at 350 nm and probe at 400 nm. Time τ3 is infinit on the time scale of the experiment.

## 4. Cartesian geometries

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -3.05158 | 0.83035 | 0.54698 |
| C | 6.0 | -3.09742 | -0.52121 | 0.36542 |
| C | 6.0 | -2.10576 | -1.32964 | -0.29854 |
| C | 6.0 | -0.78365 | -1.04180 | -0.39631 |
| C | 6.0 | -0.11092 | 0.11237 | 0.33549 |
| C | 6.0 | -0.70981 | 1.42642 | -0.10714 |
| C | 6.0 | -2.01278 | 1.72342 | 0.07826 |
| C | 6.0 | 0.22830 | -1.81055 | -1.09521 |
| C | 6.0 | 1.46432 | -1.33328 | -0.88686 |
| C | 6.0 | 1.44176 | -0.09084 | 0.01400 |
| C | 6.0 | 2.06820 | 1.04647 | -0.69202 |
| N | 7.0 | 2.56374 | 1.91797 | -1.27670 |
| C | 6.0 | 2.20408 | -0.33907 | 1.25595 |
| N | 7.0 | 2.78524 | -0.56884 | 2.23380 |
| H | 1.0 | -3.93358 | 1.30400 | 0.97423 |
| H | 1.0 | -4.01391 | -1.03255 | 0.65391 |
| H | 1.0 | -2.45717 | -2.25313 | -0.75690 |
| H | 1.0 | -0.25206 | -0.00313 | 1.41799 |
| H | 1.0 | -0.05794 | 2.16667 | -0.56227 |
| H | 1.0 | -2.33319 | 2.73593 | -0.16401 |
| H | 1.0 | -0.00099 | -2.68091 | -1.70225 |
| H | 1.0 | 2.39747 | -1.71669 | -1.28063 |

**Table 1:** DHA **5** (see Figure 1 of the manuscript). Calculated at G3MP2/6-31G(d)-level.

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 0.27147 | -0.62073 | 0.04797 |
| C | 6.0 | 0.19956 | -0.62758 | 1.42669 |
| C | 6.0 | 1.10714 | -0.06220 | 2.35388 |
| C | 6.0 | 2.21248 | 0.73732 | 2.12593 |
| C | 6.0 | 2.55681 | 1.39731 | 0.87273 |
| C | 6.0 | 2.14490 | 0.99278 | -0.41840 |
| C | 6.0 | 1.19199 | 0.06158 | -0.78355 |
| C | 6.0 | 3.23243 | 0.82862 | 3.14682 |
| C | 6.0 | 4.52351 | 0.93325 | 2.74146 |
| C | 6.0 | 4.88009 | 1.22910 | 1.33523 |
| C | 6.0 | 5.68566 | 0.25174 | 0.67480 |
| N | 7.0 | 6.28170 | -0.59273 | 0.13258 |
| C | 6.0 | 5.08219 | 2.58006 | 0.92989 |
| N | 7.0 | 5.17494 | 3.69563 | 0.59738 |
| H | 1.0 | -0.48494 | -1.20423 | -0.47246 |
| H | 1.0 | -0.60802 | -1.21034 | 1.86346 |
| H | 1.0 | 0.94844 | -0.35374 | 3.39156 |
| H | 1.0 | 2.86997 | 2.43015 | 0.95570 |
| H | 1.0 | 2.62709 | 1.52936 | -1.23416 |
| H | 1.0 | 1.05813 | -0.08787 | -1.85235 |
| H | 1.0 | 2.99185 | 0.56500 | 4.17367 |
| H | 1.0 | 5.32047 | 0.65188 | 3.42979 |

**Table 2:** TS: DHA **5** and VHF **6** (see Figure 1 of the manuscript). Calculated at G3MP2/6-31G(d)-level.

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 3.73316 | -0.32706 | 0.19816 |
| C | 6.0 | 3.26037 | 1.03464 | 0.36096 |
| C | 6.0 | 2.03191 | 1.54175 | 0.22273 |
| C | 6.0 | 0.76801 | 0.87953 | -0.11529 |
| C | 6.0 | 0.75735 | -0.42718 | -0.77393 |
| C | 6.0 | 1.71712 | -1.35280 | -0.85893 |
| C | 6.0 | 3.06550 | -1.35814 | -0.32384 |
| C | 6.0 | -0.36291 | 1.59962 | 0.07772 |
| C | 6.0 | -1.74827 | 1.23576 | -0.14344 |
| C | 6.0 | -2.40696 | 0.09300 | 0.12545 |
| C | 6.0 | -3.80836 | -0.01240 | -0.19651 |
| N | 7.0 | -4.91166 | -0.08475 | -0.45874 |
| C | 6.0 | -1.83030 | -1.03823 | 0.80182 |
| N | 7.0 | -1.39516 | -1.93406 | 1.34853 |
| H | 1.0 | 4.74536 | -0.50057 | 0.51855 |
| H | 1.0 | 4.01972 | 1.73514 | 0.66345 |
| H | 1.0 | 1.93232 | 2.59369 | 0.42518 |
| H | 1.0 | -0.16550 | -0.66981 | -1.26512 |
| H | 1.0 | 1.44947 | -2.24764 | -1.39320 |
| H | 1.0 | 3.57991 | -2.30030 | -0.39300 |
| H | 1.0 | -0.24770 | 2.62373 | 0.38827 |
| H | 1.0 | -2.36479 | 2.03185 | -0.52722 |

**Table 3:** s-*cis* VHF **6** (see Figure 1 of the manuscript). Calculated at G3MP2/6-31G(d)-level.

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -3.98385 | -0.98208 | -0.03830 |
| C | 6.0 | -2.79790 | -1.63696 | -0.12036 |
| C | 6.0 | -1.45076 | -1.13845 | -0.09663 |
| C | 6.0 | -1.01780 | 0.17936 | 0.01889 |
| C | 6.0 | -1.82499 | 1.32431 | 0.14099 |
| C | 6.0 | -3.24975 | 1.41340 | 0.17439 |
| C | 6.0 | -4.20038 | 0.44317 | 0.09970 |
| C | 6.0 | 0.43508 | 0.47376 | 0.02044 |
| C | 6.0 | 1.45417 | -0.42290 | -0.09811 |
| C | 6.0 | 2.83729 | -0.08556 | -0.09127 |
| C | 6.0 | 3.81040 | -1.09812 | -0.22195 |
| N | 7.0 | 4.59379 | -1.95238 | -0.33133 |
| C | 6.0 | 3.27370 | 1.25096 | 0.04425 |
| N | 7.0 | 3.59515 | 2.36305 | 0.15785 |
| H | 1.0 | -4.88163 | -1.59236 | -0.08019 |
| H | 1.0 | -2.86448 | -2.71846 | -0.22078 |
| H | 1.0 | -0.69234 | -1.90566 | -0.17964 |
| H | 1.0 | -1.30163 | 2.26999 | 0.22016 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -3.62461 | 2.43032 | 0.27661 |
| H | 1.0 | -5.23668 | 0.76322 | 0.14799 |
| H | 1.0 | 0.69382 | 1.52295 | 0.12664 |
| H | 1.0 | 1.25020 | -1.48232 | -0.20908 |

**Table 4:** s-*trans* VHF **6** (see Figure 1 of the manuscript). Calculated at G3MP2/6-31G(d)-level.

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -3.94884 | 0.17043 | 0.23584 |
| C | 6.0 | -3.30736 | -1.09706 | -0.02303 |
| C | 6.0 | -2.01459 | -1.37889 | -0.32067 |
| C | 6.0 | -0.85196 | -0.50568 | -0.47758 |
| C | 6.0 | -0.94049 | 0.94422 | -0.30486 |
| C | 6.0 | -1.99863 | 1.73916 | -0.00692 |
| C | 6.0 | -3.38074 | 1.40274 | 0.24265 |
| C | 6.0 | 0.34036 | -1.09098 | -0.79704 |
| C | 6.0 | 1.61905 | -0.39605 | -1.02106 |
| C | 6.0 | 2.54908 | -0.15598 | -0.06379 |
| C | 6.0 | 3.79308 | 0.49165 | -0.38214 |
| N | 7.0 | 4.79508 | 1.01807 | -0.64763 |
| C | 6.0 | 2.35039 | -0.53362 | 1.30937 |
| N | 7.0 | 2.21647 | -0.83106 | 2.42504 |
| H | 1.0 | -5.01372 | 0.11461 | 0.45104 |
| H | 1.0 | -3.97087 | -1.95796 | 0.03187 |
| H | 1.0 | -1.78660 | -2.43330 | -0.46942 |
| H | 1.0 | 0.00650 | 1.46291 | -0.43880 |
| H | 1.0 | -1.77629 | 2.80260 | 0.05874 |
| H | 1.0 | -4.02985 | 2.24728 | 0.46308 |
| H | 1.0 | 0.37367 | -2.17090 | -0.93976 |
| H | 1.0 | 1.87824 | -0.07946 | -2.03425 |

**Table 5:** TS s-*cis* VHF **6** and s-*trans* VHF **6** (see Figure 1 of the manuscript). Calculated at G3MP2/6-31G(d)-level.

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -3.01923 | -0.57613 | -0.73010 |
| C | 6.0 | -2.35521 | 0.54476 | -1.23047 |
| C | 6.0 | -1.29993 | 1.26000 | -0.66614 |
| C | 6.0 | -0.61797 | 1.05868 | 0.55225 |
| C | 6.0 | -1.02947 | 0.17438 | 1.57145 |
| C | 6.0 | -2.01806 | -0.80857 | 1.55889 |
| C | 6.0 | -2.86849 | -1.18118 | 0.51698 |
| C | 6.0 | 0.63604 | 1.79849 | 0.75961 |
| C | 6.0 | 1.81988 | 1.24382 | 0.34745 |
| C | 6.0 | 2.05856 | -0.00412 | -0.28684 |
| C | 6.0 | 3.38313 | -0.37467 | -0.62669 |
| N | 7.0 | 4.49800 | -0.66856 | -0.90399 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 1.02020 | -0.90649 | -0.59915 |
| N | 7.0 | 0.11237 | -1.63767 | -0.84419 |
| H | 1.0 | -3.75761 | -1.02608 | -1.39044 |
| H | 1.0 | -2.66306 | 0.87045 | -2.22233 |
| H | 1.0 | -0.88310 | 2.05783 | -1.27823 |
| H | 1.0 | -0.42915 | 0.23568 | 2.47742 |
| H | 1.0 | -2.09633 | -1.40439 | 2.46637 |
| H | 1.0 | -3.50413 | -2.04356 | 0.70669 |
| H | 1.0 | 0.60485 | 2.77386 | 1.23658 |
| H | 1.0 | 2.71600 | 1.83842 | 0.52762 |

**Table 6:** TS s-*cis* VHF **6** and s-*cis* VHF **6** (see Figure 1 of the manuscript). Calculated at G3MP2/6-31G(d)-level.

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 3.78397 | -0.24657 | 0.16511 |
| C | 6.0 | 3.28721 | 1.00010 | 0.43756 |
| C | 6.0 | 1.96844 | 1.51612 | 0.29248 |
| C | 6.0 | 0.78332 | 0.85927 | -0.15099 |
| C | 6.0 | 0.71128 | -0.47084 | -0.64271 |
| C | 6.0 | 1.74590 | -1.45174 | -0.73157 |
| C | 6.0 | 3.06594 | -1.38414 | -0.38080 |
| C | 6.0 | -0.39935 | 1.67194 | -0.11644 |
| C | 6.0 | -1.77613 | 1.31271 | -0.17183 |
| C | 6.0 | -2.36755 | 0.10189 | 0.04527 |
| H | 1.0 | 4.83984 | -0.40980 | 0.36845 |
| H | 1.0 | 4.00468 | 1.71674 | 0.83617 |
| H | 1.0 | 1.83956 | 2.54955 | 0.60378 |
| H | 1.0 | -0.24016 | -0.76772 | -1.06665 |
| H | 1.0 | 1.41859 | -2.40335 | -1.14943 |
| H | 1.0 | 3.66025 | -2.28155 | -0.53863 |
| H | 1.0 | -0.21667 | 2.74016 | -0.01262 |
| H | 1.0 | -2.44760 | 2.15338 | -0.35129 |
| H | 1.0 | -1.80769 | -0.78117 | 0.33121 |
| H | 1.0 | -3.44703 | 0.00108 | -0.01383 |

**Table 7:** s-*cis* CoIn VHF **6** without the CN-groups (see Figure 4 of the manuscript) at CASSCF(10,10)/6-31G(d) level.

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -3.89489 | 0.08681 | 0.22834 |
| C | 6.0 | -3.37828 | -1.07693 | -0.27182 |
| C | 6.0 | -2.03310 | -1.42009 | -0.59681 |
| C | 6.0 | -0.84794 | -0.64023 | -0.49084 |
| C | 6.0 | -0.77962 | 0.70097 | -0.01359 |
| C | 6.0 | -1.83179 | 1.54023 | 0.44948 |

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -3.17630 | 1.30244 | 0.56391 |
| C | 6.0 | 0.34870 | -1.30247 | -0.91059 |
| C | 6.0 | 1.67405 | -0.80362 | -0.92752 |
| C | 6.0 | 2.74361 | -1.53576 | -1.35396 |
| H | 1.0 | 3.74873 | -1.12681 | -1.35581 |
| H | 1.0 | 2.62643 | -2.55708 | -1.70810 |
| H | 1.0 | -4.96897 | 0.11400 | 0.39790 |
| H | 1.0 | -4.09807 | -1.87404 | -0.45463 |
| H | 1.0 | -1.89439 | -2.42672 | -0.98299 |
| H | 1.0 | 0.20326 | 1.15788 | 0.00511 |
| H | 1.0 | -1.50365 | 2.53138 | 0.76137 |
| H | 1.0 | -3.78507 | 2.11622 | 0.95145 |
| H | 1.0 | 0.22830 | -2.32554 | -1.26444 |
| H | 1.0 | 1.86068 | 0.21189 | -0.58609 |

**Table 8:** s-*trans* CoIn VHF **6** without the CN-groups (see Figure 4 of the manuscript) at CASSCF(10,10)/6-31G(d) level.

| | | | | |
|---|---|---|---|---|
| C | 6.0 | 3.76699 | -0.46817 | 0.21545 |
| C | 6.0 | 3.32617 | 0.87623 | 0.44786 |
| C | 6.0 | 2.08720 | 1.42956 | 0.30334 |
| C | 6.0 | 0.82345 | 0.84320 | -0.10276 |
| C | 6.0 | 0.76640 | -0.46120 | -0.73470 |
| C | 6.0 | 1.70970 | -1.44135 | -0.83931 |
| C | 6.0 | 3.05515 | -1.48720 | -0.34584 |
| C | 6.0 | -0.29740 | 1.66309 | 0.00359 |
| C | 6.0 | -1.69221 | 1.40375 | -0.20265 |
| C | 6.0 | -2.34834 | 0.20010 | 0.05476 |
| C | 6.0 | -3.74379 | 0.01526 | -0.19930 |
| N | 7.0 | -4.87459 | -0.18444 | -0.39806 |
| C | 6.0 | -1.72508 | -0.89386 | 0.72501 |
| N | 7.0 | -1.22476 | -1.78349 | 1.28920 |
| H | 1.0 | 4.79559 | -0.68062 | 0.49962 |
| H | 1.0 | 4.09546 | 1.55006 | 0.82062 |
| H | 1.0 | 2.01594 | 2.48187 | 0.57460 |
| H | 1.0 | -0.17790 | -0.68083 | -1.22218 |
| H | 1.0 | 1.38864 | -2.33557 | -1.36944 |
| H | 1.0 | 3.56627 | -2.43918 | -0.47168 |
| H | 1.0 | -0.08183 | 2.71035 | 0.20394 |
| C | 6.0 | -2.49502 | 2.58300 | -0.65880 |
| C | 6.0 | -3.23425 | 2.53897 | -1.85033 |
| C | 6.0 | -3.95263 | 3.65552 | -2.27834 |
| C | 6.0 | -3.94822 | 4.82857 | -1.52185 |
| C | 6.0 | -2.49306 | 3.76939 | 0.09362 |
| C | 6.0 | -3.21885 | 4.88050 | -0.33256 |
| H | 1.0 | -4.51212 | 5.69564 | -1.85542 |
| H | 1.0 | -4.51754 | 3.60552 | -3.20518 |
| H | 1.0 | -3.24054 | 1.63278 | -2.44839 |

| | | | | |
|---|---|---|---|---|
| H | 1.0 | -3.21830 | 5.78556 | 0.26937 |
| H | 1.0 | -1.94287 | 3.81231 | 1.02988 |

**Table 9:** s-*cis* VHF **4**. Calculated at B3LYP/6-31G(d)-level.

| | | | | |
|---|---|---|---|---|
| C | 6.0 | -4.28551 | -0.54351 | 0.07465 |
| C | 6.0 | -3.12999 | -1.33897 | 0.38101 |
| C | 6.0 | -1.80281 | -1.02476 | 0.35623 |
| C | 6.0 | -1.13018 | 0.21624 | 0.00621 |
| C | 6.0 | -1.87320 | 1.45436 | -0.16325 |
| C | 6.0 | -3.21199 | 1.69801 | -0.25721 |
| C | 6.0 | -4.32207 | 0.79015 | -0.20250 |
| C | 6.0 | 0.25417 | 0.32954 | -0.08493 |
| C | 6.0 | 1.28343 | -0.66810 | -0.06827 |
| C | 6.0 | 2.59987 | -0.28294 | 0.18902 |
| C | 6.0 | 3.71359 | -1.16874 | 0.06999 |
| N | 7.0 | 4.64884 | -1.85922 | -0.01504 |
| C | 6.0 | 2.92183 | 1.05789 | 0.56409 |
| N | 7.0 | 3.16973 | 2.15572 | 0.86786 |
| H | 1.0 | -5.23652 | -1.07149 | 0.10206 |
| H | 1.0 | -3.35396 | -2.36107 | 0.68181 |
| H | 1.0 | -1.13979 | -1.82604 | 0.66052 |
| H | 1.0 | -1.23839 | 2.33427 | -0.25476 |
| H | 1.0 | -3.48339 | 2.74023 | -0.41501 |
| H | 1.0 | -5.29919 | 1.23368 | -0.38202 |
| H | 1.0 | 0.62715 | 1.34860 | -0.15493 |
| C | 6.0 | 1.01681 | -2.09376 | -0.41379 |
| C | 6.0 | 1.39983 | -3.13452 | 0.44684 |
| C | 6.0 | 0.39189 | -2.41206 | -1.63183 |
| C | 6.0 | 1.15171 | -4.46343 | 0.10174 |
| C | 6.0 | 0.15902 | -3.74095 | -1.97992 |
| C | 6.0 | 0.53396 | -4.77007 | -1.11194 |
| H | 1.0 | 0.10343 | -1.61084 | -2.30631 |
| H | 1.0 | -0.31217 | -3.97425 | -2.93104 |
| H | 1.0 | 0.34943 | -5.80618 | -1.38325 |
| H | 1.0 | 1.44920 | -5.25876 | 0.77964 |
| H | 1.0 | 1.88429 | -2.89985 | 1.38978 |

**Table 10:** s-*trans* VHF **4**. Calculated at B3LYP/6-31G(d)-level.

## References

(1) Petersen, M. Å.; Broman, S. L.; Kadziola, A.; Kilså, K.; Nielsen, M. B., Dihydroazulene Photoswitches: The First Synthetic Protocol for Functionalizing the Seven-Membered Ring. *Eur. J. Org. Chem.* **2009**, *17*, 2733.

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