**Title: Reaction of the 4-Biphenylnitrenium Ion with 4-Biphenyl Azide to Produce a 4,4'-Azobisbiphenyl Stable Product: A Time-Resolved Resonance Raman and Density Functional Theory Study**

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**Description: Figure 1S.** Overview of the 354.7 nm probe wavelength $TR^3$ spectra obtained after 299.1 nm photolysis of 2 mM 4-biphenyl azide in a water:acetonitrile(60:40 by volume) mixed solvent. **Figure 2S.** Comparison of (A) the 10 ns $TR^3$ spectra from Figure 1 with 354.7 nm as the probe wavelength to (B) that obtained with 416.0 nm as the probe wavelength reported previously in reference 22. **Figure 3S.** Comparison of (A) the B3LYP/6-31g* calculated normal Raman spectrum for *trans* 4,4'-azobisbiphenyl to (B) the experimental 100 μs $TR^3$ spectrum from Figure 2 and (C) the 354.7 nm resonance Raman spectrum of synthesized 4,4'-azobisbiphenyl. **Figure 4S.** Absorption spectra of 4-biphenyl azide (dot line) and synthesized 4,4'-azobisbiphenyl (solid line). **Figure 5S.** Comparison of (A) the intermediate observed in Figures 1 and 1S to (B) the 354.7 nm probe $TR^3$ spectrum (due to the triplet 4-biphenylnitrene species-see reference 29 for details) obtained at 10 ns after photolysis of 2 mM 4-biphenyl azide in neat acetonitrile. These spectra are clearly due to difference species and this rules out the triplet 4-biphenylnitrene species being the first species observed in the spectra shown in Figures 1 and 1S. **Table 1S.** Comparison of the experimental $TR^3$ vibrational frequencies (700~1600 $cm^{-1}$) for the intermediate to those obtained from B3LYP/6-31g* calculations for the *trans* azo cation. **Table 2S.** Comparison of the experimental $TR^3$ vibrational frequencies (700~1600 $cm^{-1}$) for the intermediate to those obtained from the B3LYP/6-31g* calculations for the *cis* azo cation.

Cartesian coordinates, total energies, and vibrational zero-point energies for the optimized geometry from the B3lyp/6-31g* calculations for the species of interest (**RC1: *cis* azide nitrenium ion complex, TS1, PC1, RC2: *tran*Azide nitrenium ion complex, TS2: *trans* transition state, PC2: *trans* 4,4'-azobisbiphenyl cation with nitrogen gas, TS3, PC3a, PC3b, TS4, PC4, *Cis* azo and *Trans* azo).**

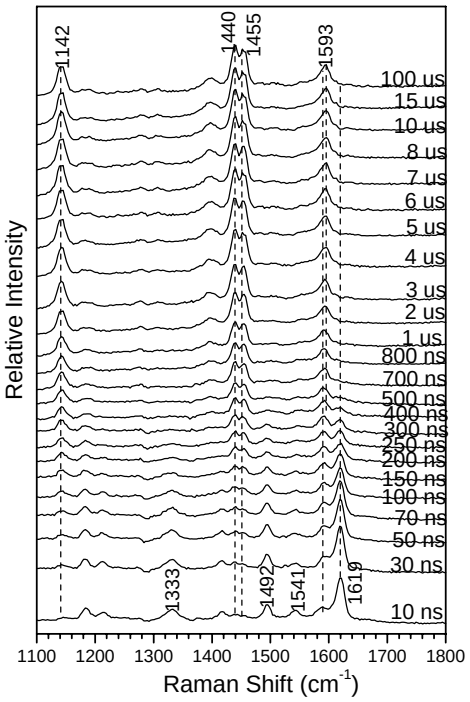


**Figure 1S.** Overview of the 354.7 nm probe wavelength $TR^3$ spectra obtained after 299.1 nm photolysis of 2 mM 4-biphenyl azide in a water:acetonitrile(60:40 by volume) mixed solvent.

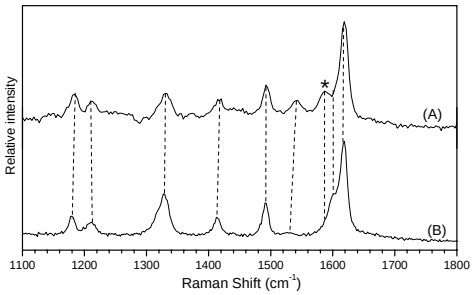


**Figure 2S.** Comparison of (A) the 10 ns $TR^3$ spectra from Figure 1 with 354.7 nm as the probe wavelength to (B) that obtained with 416.0 nm as the probe wavelength reported previously in reference 22.

Since photolysis of 4-biphenyl azide in mixed aqueous solution has previously been observed to produce the 4-biphenylnitrenium ion on the nanosecond time scale[22], we tentatively assign the early time species in Figures 1 and 1S at early times (see the 10 ns spectra ) to the 4-biphenylnitrenium ion. Figure 2S shows a comparison of the 10 ns 354.7 nm probe $TR^3$ spectrum from Figure 1 to a 10 ns 416.0 nm probe $TR^3$ spectrum previously reported for the 4-biphenylnitrenium ion[22] that was obtained after 266 nm photolysis of 4-biphenyl azide in a water:acetonitrile (60:40 by volume) mixed solution. Examination of Figure 2S shows that the two $TR^3$ spectra are almost identical with an exception for the band labeled with a star symbol, which comes from the contribution of the second species (see the kinetic analysis section for more details). Other modest variations between the two Raman spectra in the relative intensities can be easily attributed to the difference in the excitation wavelengths used to generate the $TR^3$ spectra. This indicates the $TR^3$ spectra are due to the same species and confirms that the first species seen in the $TR^3$ spectra of Figures 1 and 1S (see the 10 ns spectra) are due to the 4- biphenylnitrenium ion.

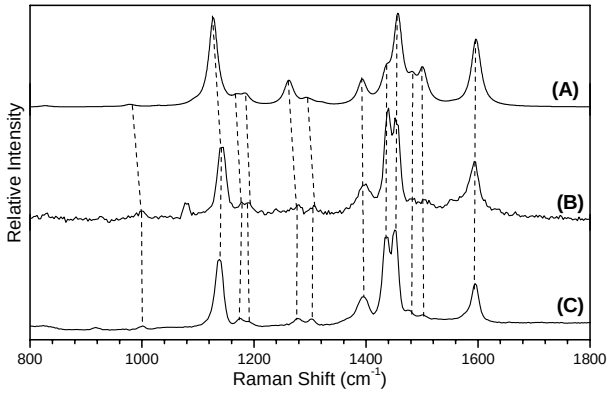


**Figure 3S.** Comparison of (A) the B3LYP/6-31g* calculated normal Raman spectrum for *trans* 4,4'-azobisbiphenyl to (B) the experimental 100 μs $TR^3$ spectrum from Figure 2 and (C) the 354.7 nm resonance Raman spectrum of synthesized 4,4'-azobisbiphenyl.

Comparison of the experimental vibrational frequencies to those predicted from DFT or *ab initio* calculations for probable intermediates have proven useful to identify and assign time-resolved infrared (TRIR) and $TR^3$ spectra to arylnitrenium ions, arylnitrenes, and arylnitrene photoproducts[16,17,26,28]. Here, B3LYP/6-31g* calculations were performed to predict the total energy, optimized geometry and vibrational frequencies for *trans* 4,4-azobisbiphenyl. Figure 3S compares the experimental 100 μs $TR^3$ spectrum from Fig. 1S to the B3LYP/6-31g* calculated normal Raman spectrum whose relative intensities were convoluted with a Lorentzian function. Comparison of the experimental $TR^3$ spectrum to the calculated *trans* 4,4-azobisbiphenyl spectrum reveals reasonable agreement with the calculated normal Raman spectrum of 4,4-azobisbiphenyl with some moderate differences in the relative intensities that can be easily accounted for by the fact that the experimental spectrum is resonantly enhanced while the calculated spectrum is for a normal Raman spectrum. To unequivocally confirm this assignment, we made the 4,4-azobisbiphenyl compound using a different synthetic method and compared its 354.7 nm resonance Raman spectrum to that of the experimental 100 μs $TR^3$ spectrum (from Fig. 1S) and this comparison is shown in Fig. 3S. The two different Raman spectra are essentially identical within experimental uncertainty and this unambiguously confirms the assignment of the third species in $TR^3$ spectra to *trans* 4,4-azobisbiphenyl.

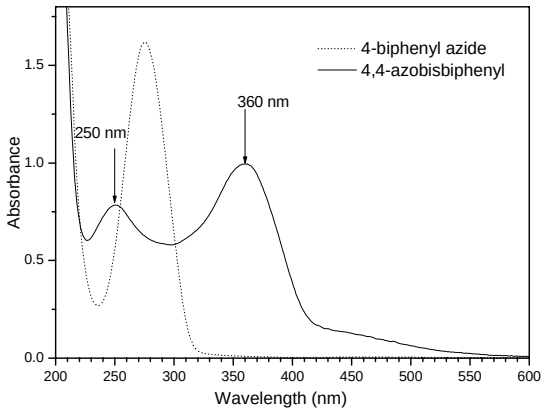


**Figure 4S.** Absorption spectra of 4-biphenyl azide (dot line) and synthesized 4,4'-azobisbiphenyl (solid line).

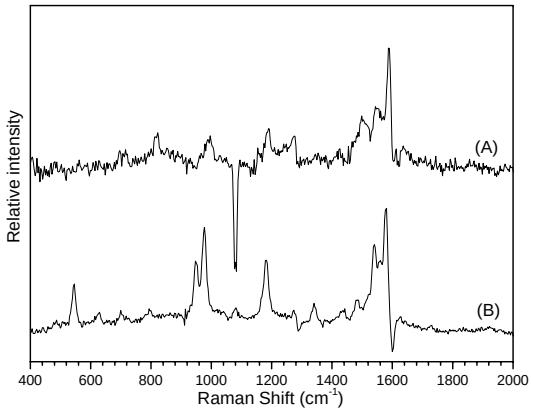


**Figure 5S.** Comparison of (A) the intermediate observed in Figures 1 and 1S to (B) the 354.7 nm probe TR[3] spectrum (due to the triplet 4-biphenylnitrene species-see reference 29 for details) obtained at 10 ns after photolysis of 2 mM 4-biphenyl azide in neat acetonitrile. These spectra are clearly due to difference species and this rules out the triplet 4-biphenylnitrene species being the first species observed in the spectra shown in Figures 1 and 1S.

**Table 1S.** Comparison of the experimental TR[3] vibrational frequencies (700~1600 $cm^{-1}$) for the intermediate to those obtained from B3LYP/6-31g* calculations for the *trans* azo cation

| | **Calculated *trans* azo cation** | | | **Experimental** |
|---|---|---|---|---|
| | **Vibrational Mode** | **Raman Activity** | **B3LYP /6-31g* calc. (in $cm^{-1}$)** | **Raman frequency shift (in $cm^{-1}$)** |
| $\nu_{39}$ | CCC bend (rings A and D, in the ring plane) | 98 | 706 | 706 |
| $\nu_{47}$ | CCCbend (rings B and C, in the ring plane) + C-H bend (rings A and D) | 135 | 820 | 819 |
| $\nu_{66}$ | CCC bend (rings A and B, in the ring plane) | 1107 | 983 | |
| $\nu_{67}$ | CCC bend (ring D, in the ring plane) + C-H bend (ring C, in the ring plane) | 520 | 996 | 993 |
| $\nu_{75}$ | C-H bend (ring A, in the ring plane) | 86 | 1158 | |
| $\nu_{76}$ | C-H bend (ring D, in the ring plane) | 33 | 1160 | 1154 |
| $\nu_{77}$ | C-H bend (rings B and C, in the ring plane) + N1-C stretch | 4757 | 1163 | |
| $\nu_{79}$ | C-H bend (ring A, in the ring plane) + N-Cstretch | 2724 | 1180 | 1189 |
| $\nu_{80}$ | C-H bend (ring D, in the ring plane) + N-C stretch | 2440 | 1182 | |
| $\nu_{85}$ | N-C stretch + C-C stretch | 12446 | 1276 | 1275 |
| $\nu_{92}$ | C-C stretch | 2838 | 1340 | 1350 |
| $\nu_{93}$ | N=N stretch + N-H bend | 58649 | 1375 | 1374 |
| $\nu_{94}$ | C-C aromatic stretch (ring B strong) + N-H bend | 452 | 1418 | 1423 |
| $\nu_{98}$ | C-C stretch (all rings) + N-C stretch | 1206 | 1475 | 1475 |
| $\nu_{99}$ | C-C stretch (all rings) + N-C stretch | 1062 | 1479 | |
| $\nu_{100}$ | C-C stretch (all rings) + N-C stretch + N-H bend | 1463 | 1501 | |
| $\nu_{101}$ | C-C stretch (all rings) + N-C stretch + N-H bend | 686 | 1504 | 1501 |
| $\nu_{102}$ | C-C stretch (rings B and C strong) + N-H bend | 5035 | 1510 | |
| $\nu_{103}$ | C-C aromatic stretch (rings B and C strong) + N-H bend | 10160 | 1535 | 1547 |
| $\nu_{106}$ | C-C aromatic stretch (all rings) + N-H bend | 1674 | 1578 | |
| $\nu_{107}$ | C-C aromatic stretch (mainly rings A and B) + N-H bend | 23952 | 1584 | 1587 |

**Table 2S.** Comparison of the experimental TR[3] vibrational frequencies (700~1600 $cm^{-1}$) for the intermediate to those obtained from the B3LYP/6-31g* calculations for the *cis* azo cation

| | Calculated *cis* azo cation | | | Experimental |
|---|---|---|---|---|
| | Vibrational Mode | Raman Activity | B3LYP /6-31g* calc. (in $cm^{-1}$) | Raman frequency shift (in $cm^{-1}$) |
| $\nu_{44}$ | CCC bend + C-H bend + O-H bend | 9 | 711 | 706 |
| $\nu_{50}$ | C-H bend (ring C) | 46 | 817 | |
| $\nu_{51}$ | C-H bend (ring B) | 58 | 822 | 819 |
| $\nu_{71}$ | O-H bend + N-H bend + CCC bend (in the ring plane) | 73 | 995 | 993 |
| $\nu_{83}$ | C-H bend (in the ring plane) + C-N stretch + O-H bend | 423 | 1160 | 1154 |
| $\nu_{87}$ | C-H bend (in the ring plane) + C-N stretch + O-H bend | 16 | 1193 | 1189 |
| $\nu_{90}$ | C-C stretch (mainly rings A and B) | 873 | 1264 | |
| $\nu_{91}$ | C-C stretch (mainly rings C and D) | 6 | 1266 | |
| $\nu_{92}$ | C-C stretch (all rings) | 10 | 1287 | 1275 |
| $\nu_{98}$ | N-N stretch + O-H bend | 1500 | 1344 | 1350 |
| $\nu_{99}$ | C-C stretch (rings C and D) + N-H bend | 61 | 1390 | 1374 |
| $\nu_{100}$ | C-C stretch (rings A and B) +N-H bend | 52 | 1403 | |
| $\nu_{101}$ | C-C stretch + N-H bend | 8 | 1437 | 1423 |
| $\nu_{104}$ | C-C stretch | 11 | 1475 | |
| $\nu_{105}$ | C-C stretch (all rings) + N-H bend | 194 | 1478 | 1475 |
| $\nu_{106}$ | C-C stretch (rings C and D) + N-H bend | 59 | 1497 | |
| $\nu_{107}$ | C-C stretch (all rings) + N-H bend | 24 | 1500 | 1501 |
| $\nu_{108}$ | C-C aromatic stretch (rings A and B) + N-H bend | 43 | 1540 | |
| $\nu_{109}$ | C-C aromatic stretch (rings C and D) + N-H bend | 36 | 1562 | 1547 |
| $\nu_{112}$ | C-C aromatic stretch (all rings) + N-H bend | 2110 | 1593 | |
| $\nu_{113}$ | C-C aromatic stretch (all rings) + N-H bend | 2189 | 1594 | 1587 |

Cartesian coordinates, total energies, and vibrational zero-point energies for the optimized geometry from the B3lyp/6-31g* calculations for the species presented in the paper.

**RC1: *cis* azide nitrenium ion complex**

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -3.163092 | -1.369627 | -1.176998 |
| 2 | 6 | 0 | -2.564752 | -2.193841 | -0.190837 |
| 3 | 6 | 0 | -3.413604 | -2.859093 | 0.729522 |
| 4 | 6 | 0 | -4.791716 | -2.716006 | 0.655980 |
| 5 | 6 | 0 | -5.360010 | -1.889155 | -0.319951 |
| 6 | 6 | 0 | -4.540375 | -1.212573 | -1.230906 |
| 7 | 6 | 0 | -1.121165 | -2.358825 | -0.129890 |
| 8 | 6 | 0 | -0.305485 | -2.153274 | -1.285384 |

| | | | | | |
|---|---|---|---|---|---|
| 9 | 6 | 0 | 1.048507 | -2.334224 | -1.238534 |
| 10 | 6 | 0 | 1.710072 | -2.734815 | -0.011871 |
| 11 | 6 | 0 | 0.875870 | -2.903860 | 1.164522 |
| 12 | 6 | 0 | -0.476745 | -2.738855 | 1.094197 |
| 13 | 7 | 0 | 3.005478 | -2.914413 | -0.048652 |
| 14 | 7 | 0 | 3.996926 | -0.638488 | 0.606199 |
| 15 | 7 | 0 | 4.848487 | -0.776780 | -0.301994 |
| 16 | 7 | 0 | 5.670156 | -1.026662 | -1.041901 |
| 17 | 6 | 0 | 2.990903 | 0.325655 | 0.426882 |
| 18 | 6 | 0 | 2.202823 | 0.614336 | 1.555757 |
| 19 | 6 | 0 | 1.187738 | 1.554158 | 1.468819 |
| 20 | 6 | 0 | 0.913646 | 2.234758 | 0.263403 |
| 21 | 6 | 0 | 1.708925 | 1.919460 | -0.859892 |
| 22 | 6 | 0 | 2.724399 | 0.978280 | -0.792464 |
| 23 | 6 | 0 | -0.160000 | 3.246383 | 0.180572 |
| 24 | 6 | 0 | -1.320057 | 3.137139 | 0.971874 |
| 25 | 6 | 0 | -2.329578 | 4.092610 | 0.895292 |
| 26 | 6 | 0 | -2.202041 | 5.181654 | 0.029486 |
| 27 | 6 | 0 | -1.056361 | 5.306452 | -0.760253 |
| 28 | 6 | 0 | -0.048153 | 4.349188 | -0.688340 |
| 29 | 1 | 0 | -2.987506 | 5.929547 | -0.026291 |
| 30 | 1 | 0 | -3.219148 | 3.986623 | 1.509588 |
| 31 | 1 | 0 | -1.444190 | 2.283491 | 1.632099 |
| 32 | 1 | 0 | -0.943093 | 6.157425 | -1.425411 |
| 33 | 1 | 0 | 0.622816 | 1.800609 | 2.361839 |
| 34 | 1 | 0 | 2.434055 | 0.127284 | 2.497655 |
| 35 | 1 | 0 | 3.318466 | 0.756815 | -1.674918 |
| 36 | 1 | 0 | 3.362433 | -3.200780 | 0.870271 |
| 37 | 1 | 0 | 1.668707 | -2.222445 | -2.121849 |
| 38 | 1 | 0 | -0.775111 | -1.899945 | -2.228476 |
| 39 | 1 | 0 | 1.351727 | -3.174974 | 2.103618 |
| 40 | 1 | 0 | -2.542249 | -0.815896 | -1.872786 |
| 41 | 1 | 0 | -4.980343 | -0.562087 | -1.980163 |
| 42 | 1 | 0 | -6.438509 | -1.773331 | -0.371138 |
| 43 | 1 | 0 | -5.427750 | -3.251878 | 1.353392 |
| 44 | 1 | 0 | -2.993385 | -3.529790 | 1.471087 |
| 45 | 1 | 0 | -1.073261 | -2.856430 | 1.991389 |
| 46 | 1 | 0 | 0.851747 | 4.479390 | -1.281889 |
| 47 | 1 | 0 | 1.508761 | 2.405232 | -1.809485 |

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E(RB+HF-LYP) = -1144.67153996 A.U. after 13 cycles
Zero-point correction= 0.373146 (Hartree/Particle)

**TS1**

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -3.950751 | -2.202514 | 1.147011 |
| 2 | 6 | 0 | -3.740323 | -1.445763 | -0.019787 |
| 3 | 6 | 0 | -4.281456 | -1.912309 | -1.231388 |
| 4 | 6 | 0 | -5.012308 | -3.097057 | -1.272998 |
| 5 | 6 | 0 | -5.209236 | -3.841262 | -0.107742 |
| 6 | 6 | 0 | -4.674790 | -3.391293 | 1.101464 |
| 7 | 6 | 0 | -2.965302 | -0.187008 | 0.026326 |
| 8 | 6 | 0 | -3.028837 | 0.664759 | 1.149664 |
| 9 | 6 | 0 | -2.309238 | 1.851138 | 1.199703 |
| 10 | 6 | 0 | -1.507013 | 2.200024 | 0.109097 |
| 11 | 6 | 0 | -1.409448 | 1.377109 | -1.018425 |
| 12 | 6 | 0 | -2.142291 | 0.197674 | -1.051629 |
| 13 | 7 | 0 | -0.740355 | 3.421498 | 0.203527 |
| 14 | 7 | 0 | -0.905178 | 4.277988 | -0.722083 |
| 15 | 7 | 0 | -0.998687 | 5.105843 | -1.482074 |
| 16 | 7 | 0 | 0.781039 | 3.549466 | 0.753723 |
| 17 | 6 | 0 | 1.496380 | 2.349636 | 0.572308 |
| 18 | 6 | 0 | 2.246092 | 2.194487 | -0.609165 |
| 19 | 6 | 0 | 3.018944 | 1.060568 | -0.794980 |
| 20 | 6 | 0 | 3.080584 | 0.046171 | 0.187865 |
| 21 | 6 | 0 | 2.321948 | 0.217661 | 1.365525 |
| 22 | 6 | 0 | 1.529949 | 1.340091 | 1.552020 |
| 23 | 6 | 0 | 3.920543 | -1.152608 | -0.007220 |
| 24 | 6 | 0 | 4.551509 | -1.774892 | 1.086475 |
| 25 | 6 | 0 | 5.347095 | -2.902218 | 0.900980 |
| 26 | 6 | 0 | 5.520617 | -3.436080 | -0.378013 |
| 27 | 6 | 0 | 4.897754 | -2.831691 | -1.472569 |
| 28 | 6 | 0 | 4.109836 | -1.698476 | -1.290774 |
| 29 | 1 | 0 | -5.777247 | -4.766201 | -0.141605 |
| 30 | 1 | 0 | -4.816929 | -3.969899 | 2.009397 |
| 31 | 1 | 0 | -3.516627 | -1.878718 | 2.088699 |
| 32 | 1 | 0 | -5.435211 | -3.435433 | -2.214243 |
| 33 | 1 | 0 | -3.680802 | 0.408907 | 1.978045 |
| 34 | 1 | 0 | -2.387193 | 2.513228 | 2.056608 |
| 35 | 1 | 0 | -0.763567 | 1.647489 | -1.848388 |
| 36 | 1 | 0 | 0.559839 | 3.696257 | 1.740724 |
| 37 | 1 | 0 | 2.247090 | 2.992269 | -1.346440 |
| 38 | 1 | 0 | 3.628008 | 0.973254 | -1.688463 |
| 39 | 1 | 0 | 0.941109 | 1.444733 | 2.460233 |
| 40 | 1 | 0 | 3.610345 | -1.254116 | -2.146852 |
| 41 | 1 | 0 | 5.022304 | -3.246754 | -2.468350 |
| 42 | 1 | 0 | 6.139447 | -4.316906 | -0.521322 |
| 43 | 1 | 0 | 5.839009 | -3.359846 | 1.754150 |

| | | | | | |
|---|---|---|---|---|---|
| 44 | 1 | 0 | 4.451525 | -1.351545 | 2.081603 |
| 45 | 1 | 0 | 2.333260 | -0.556258 | 2.125613 |
| 46 | 1 | 0 | -4.161678 | -1.327522 | -2.139002 |
| 47 | 1 | 0 | -2.051975 | -0.453375 | -1.914548 |

E(RB+HF-LYP) = -1144.65208913 A.U. after 7 cycles
Zero-point correction= 0.373386 (Hartree/Particle)

**PC1:**
Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -4.728223 | -1.518344 | 1.244545 |
| 2 | 6 | 0 | -4.367502 | -1.109254 | -0.051370 |
| 3 | 6 | 0 | -4.943001 | -1.772983 | -1.149104 |
| 4 | 6 | 0 | -5.851309 | -2.811474 | -0.955999 |
| 5 | 6 | 0 | -6.197693 | -3.209977 | 0.336676 |
| 6 | 6 | 0 | -5.632326 | -2.560701 | 1.436084 |
| 7 | 6 | 0 | -3.402797 | -0.004052 | -0.254991 |
| 8 | 6 | 0 | -3.374922 | 1.105715 | 0.614428 |
| 9 | 6 | 0 | -2.480440 | 2.151251 | 0.421676 |
| 10 | 6 | 0 | -1.574050 | 2.100622 | -0.643934 |
| 11 | 6 | 0 | -1.575672 | 1.006312 | -1.515553 |
| 12 | 6 | 0 | -2.489653 | -0.025173 | -1.325998 |
| 13 | 7 | 0 | -0.685458 | 3.214501 | -0.843429 |
| 14 | 7 | 0 | 0.559697 | 3.095154 | -0.087992 |
| 15 | 7 | 0 | 0.669967 | 4.010864 | 0.800971 |
| 16 | 7 | 0 | 0.777390 | 4.830144 | 1.565795 |
| 17 | 6 | 0 | 1.500905 | 1.991139 | -0.022749 |
| 18 | 6 | 0 | 2.610913 | 2.014211 | -0.873126 |
| 19 | 6 | 0 | 3.497954 | 0.946680 | -0.839418 |
| 20 | 6 | 0 | 3.296491 | -0.148794 | 0.027359 |
| 21 | 6 | 0 | 2.162314 | -0.133591 | 0.865841 |
| 22 | 6 | 0 | 1.263493 | 0.925422 | 0.851320 |
| 23 | 6 | 0 | 4.250924 | -1.277620 | 0.056999 |
| 24 | 6 | 0 | 4.903792 | -1.696606 | -1.116567 |
| 25 | 6 | 0 | 5.801145 | -2.761067 | -1.088008 |
| 26 | 6 | 0 | 6.069546 | -3.420170 | 0.113658 |
| 27 | 6 | 0 | 5.431465 | -3.011855 | 1.287029 |
| 28 | 6 | 0 | 4.526738 | -1.953670 | 1.259415 |
| 29 | 1 | 0 | 6.772618 | -4.247490 | 0.135650 |
| 30 | 1 | 0 | 6.286458 | -3.080390 | -2.005467 |
| 31 | 1 | 0 | 4.682704 | -1.211484 | -2.063071 |
| 32 | 1 | 0 | 5.644147 | -3.513424 | 2.226387 |

| | | | | | |
|---|---|---|---|---|---|
| 33 | 1 | 0 | 4.379246 | 0.974377 | -1.471110 |
| 34 | 1 | 0 | 2.784646 | 2.859559 | -1.532425 |
| 35 | 1 | 0 | 0.385742 | 0.918690 | 1.489301 |
| 36 | 1 | 0 | -0.384594 | 3.302211 | -1.813989 |
| 37 | 1 | 0 | -2.506910 | 3.023906 | 1.068278 |
| 38 | 1 | 0 | -4.098021 | 1.169160 | 1.421033 |
| 39 | 1 | 0 | -0.866870 | 0.959472 | -2.338889 |
| 40 | 1 | 0 | -4.275716 | -1.038717 | 2.108127 |
| 41 | 1 | 0 | -5.891214 | -2.870157 | 2.444517 |
| 42 | 1 | 0 | -6.905087 | -4.020301 | 0.486464 |
| 43 | 1 | 0 | -6.295823 | -3.303997 | -1.815898 |
| 44 | 1 | 0 | -4.705941 | -1.451845 | -2.159465 |
| 45 | 1 | 0 | -2.474484 | -0.875618 | -1.999819 |
| 46 | 1 | 0 | 4.060350 | -1.627154 | 2.184567 |
| 47 | 1 | 0 | 1.969027 | -0.977575 | 1.519110 |

E(RB+HF-LYP) = -1144.65330567 A.U. after 10 cycles
Zero-point correction= 0.374414 (Hartree/Particle)

**RC2: *tran*Azide nitrenium ion complex**

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -6.300122 | 1.673478 | -0.289862 |
| 2 | 6 | 0 | -6.042923 | 0.279352 | -0.229502 |
| 3 | 6 | 0 | -7.138422 | -0.593147 | -0.001669 |
| 4 | 6 | 0 | -8.424282 | -0.094934 | 0.145255 |
| 5 | 6 | 0 | -8.652002 | 1.285458 | 0.094153 |
| 6 | 6 | 0 | -7.584739 | 2.166581 | -0.117747 |
| 7 | 6 | 0 | -4.697535 | -0.240769 | -0.394689 |
| 8 | 6 | 0 | -3.697408 | 0.512060 | -1.090315 |
| 9 | 6 | 0 | -2.430727 | 0.030007 | -1.255207 |
| 10 | 6 | 0 | -2.054218 | -1.281539 | -0.744503 |
| 11 | 6 | 0 | -3.073406 | -2.021536 | -0.016387 |
| 12 | 6 | 0 | -4.332444 | -1.522934 | 0.136494 |
| 13 | 7 | 0 | -0.889377 | -1.848237 | -0.895131 |
| 14 | 7 | 0 | 0.760118 | -0.879719 | 1.201673 |
| 15 | 7 | 0 | -0.108729 | -0.006458 | 1.323831 |
| 16 | 7 | 0 | -1.032967 | 0.655757 | 1.438601 |
| 17 | 6 | 0 | 2.083186 | -0.518891 | 0.874731 |
| 18 | 6 | 0 | 2.493891 | 0.796533 | 0.597967 |
| 19 | 6 | 0 | 3.821689 | 1.046617 | 0.289010 |
| 20 | 6 | 0 | 4.776575 | 0.007596 | 0.233987 |

| | | | | | |
|---|---|---|---|---|---|
| 21 | 6 | 0 | 4.334187 | -1.304265 | 0.508990 |
| 22 | 6 | 0 | 3.011898 | -1.570176 | 0.826744 |
| 23 | 6 | 0 | 6.187666 | 0.286319 | -0.096833 |
| 24 | 6 | 0 | 6.965059 | -0.656912 | -0.797469 |
| 25 | 6 | 0 | 8.295380 | -0.393187 | -1.109221 |
| 26 | 6 | 0 | 8.881767 | 0.814715 | -0.721853 |
| 27 | 6 | 0 | 8.125369 | 1.759437 | -0.023254 |
| 28 | 6 | 0 | 6.792667 | 1.500854 | 0.282693 |
| 29 | 1 | 0 | 8.577969 | 2.695312 | 0.291091 |
| 30 | 1 | 0 | 6.226329 | 2.230295 | 0.854262 |
| 31 | 1 | 0 | 6.514217 | -1.587565 | -1.129167 |
| 32 | 1 | 0 | 8.874685 | -1.127715 | -1.660947 |
| 33 | 1 | 0 | 9.921187 | 1.017966 | -0.962125 |
| 34 | 1 | 0 | 5.048368 | -2.120929 | 0.505665 |
| 35 | 1 | 0 | 2.680253 | -2.578240 | 1.052328 |
| 36 | 1 | 0 | 1.780119 | 1.615546 | 0.628859 |
| 37 | 1 | 0 | 4.124333 | 2.062879 | 0.058678 |
| 38 | 1 | 0 | -1.692204 | 0.600965 | -1.812164 |
| 39 | 1 | 0 | -3.961225 | 1.467864 | -1.527241 |
| 40 | 1 | 0 | -5.062020 | -2.088382 | 0.703941 |
| 41 | 1 | 0 | -2.784214 | -2.984398 | 0.392128 |
| 42 | 1 | 0 | -6.986304 | -1.666672 | 0.010666 |
| 43 | 1 | 0 | -9.253770 | -0.778350 | 0.296443 |
| 44 | 1 | 0 | -9.658440 | 1.673572 | 0.219206 |
| 45 | 1 | 0 | -7.759913 | 3.237382 | -0.143874 |
| 46 | 1 | 0 | -5.482011 | 2.373010 | -0.421504 |
| 47 | 1 | 0 | -0.257303 | -1.256249 | -1.448137 |

E(UB+HF-LYP) = -1144.67058417 A.U. after 17 cycles
Zero-point correction= 0.372815 (Hartree/Particle)

**TS2: *trans* transition state**

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -6.743118 | -1.219052 | 0.606992 |
| 2 | 6 | 0 | -6.143202 | -0.074884 | 0.051672 |
| 3 | 6 | 0 | -6.967686 | 0.998677 | -0.329438 |
| 4 | 6 | 0 | -8.348770 | 0.927999 | -0.162857 |
| 5 | 6 | 0 | -8.931092 | -0.212871 | 0.393326 |
| 6 | 6 | 0 | -8.123783 | -1.285101 | 0.778917 |
| 7 | 6 | 0 | -4.675987 | -0.002093 | -0.128057 |

| | | | | | |
|---|---|---|---|---|---|
| 8 | 6 | 0 | -3.983723 | 1.212990 | 0.046366 |
| 9 | 6 | 0 | -2.606196 | 1.290039 | -0.111932 |
| 10 | 6 | 0 | -1.899749 | 0.138846 | -0.479793 |
| 11 | 6 | 0 | -2.552106 | -1.083747 | -0.658084 |
| 12 | 6 | 0 | -3.927872 | -1.144389 | -0.477861 |
| 13 | 7 | 0 | -0.478656 | 0.146885 | -0.647918 |
| 14 | 7 | 0 | 0.136008 | 1.221121 | -0.969749 |
| 15 | 7 | 0 | 1.091734 | 1.848912 | -1.033512 |
| 16 | 7 | 0 | 0.411705 | -0.642385 | 0.621788 |
| 17 | 6 | 0 | 1.761801 | -0.444112 | 0.477553 |
| 18 | 6 | 0 | 2.486342 | 0.500654 | 1.261918 |
| 19 | 6 | 0 | 3.861534 | 0.582542 | 1.162967 |
| 20 | 6 | 0 | 4.578822 | -0.226139 | 0.250511 |
| 21 | 6 | 0 | 3.842236 | -1.138339 | -0.556891 |
| 22 | 6 | 0 | 2.475626 | -1.252013 | -0.450256 |
| 23 | 6 | 0 | 6.039804 | -0.130721 | 0.137355 |
| 24 | 6 | 0 | 6.809738 | -1.250610 | -0.242145 |
| 25 | 6 | 0 | 8.194018 | -1.160617 | -0.337992 |
| 26 | 6 | 0 | 8.838174 | 0.051500 | -0.074574 |
| 27 | 6 | 0 | 8.089759 | 1.173218 | 0.294078 |
| 28 | 6 | 0 | 6.707062 | 1.082888 | 0.407400 |
| 29 | 1 | 0 | -8.971563 | 1.761207 | -0.475016 |
| 30 | 1 | 0 | -6.530236 | 1.879243 | -0.791459 |
| 31 | 1 | 0 | -6.123731 | -2.048130 | 0.937415 |
| 32 | 1 | 0 | -8.569035 | -2.171717 | 1.220738 |
| 33 | 1 | 0 | -10.007794 | -0.266285 | 0.524918 |
| 34 | 1 | 0 | -4.439092 | -2.086264 | -0.646240 |
| 35 | 1 | 0 | -1.985887 | -1.963454 | -0.944428 |
| 36 | 1 | 0 | -2.088715 | 2.233140 | 0.044061 |
| 37 | 1 | 0 | -4.529404 | 2.102296 | 0.343653 |
| 38 | 1 | 0 | 1.954974 | 1.117018 | 1.983509 |
| 39 | 1 | 0 | 4.398898 | 1.262007 | 1.814874 |
| 40 | 1 | 0 | 4.368516 | -1.747297 | -1.283510 |
| 41 | 1 | 0 | 1.922367 | -1.962465 | -1.056457 |
| 42 | 1 | 0 | 6.327539 | -2.206687 | -0.420252 |
| 43 | 1 | 0 | 8.772760 | -2.037032 | -0.613033 |
| 44 | 1 | 0 | 9.918698 | 0.121904 | -0.156440 |
| 45 | 1 | 0 | 8.585451 | 2.119538 | 0.487718 |
| 46 | 1 | 0 | 6.137077 | 1.970149 | 0.664983 |
| 47 | 1 | 0 | 0.043833 | -0.106885 | 1.415640 |

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E(UB+HF-LYP) = -1144.65434450 A.U. after 4 cycles
Zero-point correction= 0.372886 (Hartree/Particle)

**PC2: *trans* 4,4'-azobisbiphenyl cation with nitrogen gas**

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 6.740028 | -1.451839 | -0.462391 |
| 2 | 6 | 0 | 6.079000 | -0.305021 | 0.025834 |
| 3 | 6 | 0 | 6.860582 | 0.758827 | 0.523776 |
| 4 | 6 | 0 | 8.248340 | 0.674435 | 0.538191 |
| 5 | 6 | 0 | 8.887362 | -0.465942 | 0.043092 |
| 6 | 6 | 0 | 8.128631 | -1.526288 | -0.460328 |
| 7 | 6 | 0 | 4.613115 | -0.217058 | 0.014771 |
| 8 | 6 | 0 | 3.950884 | 1.026245 | -0.104046 |
| 9 | 6 | 0 | 2.573089 | 1.101882 | -0.111565 |
| 10 | 6 | 0 | 1.781358 | -0.068436 | 0.004001 |
| 11 | 6 | 0 | 2.435023 | -1.324958 | 0.125024 |
| 12 | 6 | 0 | 3.810490 | -1.386030 | 0.126764 |
| 13 | 7 | 0 | 0.433323 | 0.160881 | -0.015768 |
| 14 | 7 | 0 | -0.395270 | -0.807407 | 0.094192 |
| 15 | 6 | 0 | -1.786658 | -0.651751 | 0.077683 |
| 16 | 6 | 0 | -2.571136 | -1.809314 | 0.211228 |
| 17 | 6 | 0 | -3.951437 | -1.703491 | 0.198771 |
| 18 | 6 | 0 | -4.587887 | -0.451864 | 0.053341 |
| 19 | 6 | 0 | -3.766875 | 0.693911 | -0.078809 |
| 20 | 6 | 0 | -2.386547 | 0.610192 | -0.069093 |
| 21 | 6 | 0 | -6.057759 | -0.341079 | 0.037562 |
| 22 | 6 | 0 | -6.700440 | 0.802549 | 0.550979 |
| 23 | 6 | 0 | -8.088482 | 0.902259 | 0.541791 |
| 24 | 6 | 0 | -8.863148 | -0.131770 | 0.010157 |
| 25 | 6 | 0 | -8.240321 | -1.270040 | -0.508153 |
| 26 | 6 | 0 | -6.853033 | -1.377092 | -0.490414 |
| 27 | 7 | 0 | -0.576620 | 3.923369 | -0.408644 |
| 28 | 7 | 0 | 0.294851 | 4.600816 | -0.465859 |
| 29 | 1 | 0 | 8.833468 | 1.495497 | 0.941034 |
| 30 | 1 | 0 | 6.377977 | 1.637954 | 0.939311 |
| 31 | 1 | 0 | 6.166669 | -2.270883 | -0.885615 |
| 32 | 1 | 0 | 8.621149 | -2.408969 | -0.856711 |
| 33 | 1 | 0 | 9.971474 | -0.528057 | 0.049892 |
| 34 | 1 | 0 | 4.292993 | -2.349145 | 0.250950 |
| 35 | 1 | 0 | 1.881319 | -2.254784 | 0.228941 |
| 36 | 1 | 0 | 2.063063 | 2.053447 | -0.216897 |
| 37 | 1 | 0 | 4.531358 | 1.933882 | -0.225108 |
| 38 | 1 | 0 | -2.101561 | -2.782623 | 0.336956 |
| 39 | 1 | 0 | -4.549733 | -2.597768 | 0.333454 |
| 40 | 1 | 0 | -4.228918 | 1.664552 | -0.222715 |
| 41 | 1 | 0 | -1.772178 | 1.495328 | -0.184589 |
| 42 | 1 | 0 | -6.112868 | 1.600862 | 0.994596 |

| | | | | | |
|---|---|---|---|---|---|
| 43 | 1 | 0 | -8.567258 | 1.784640 | 0.955772 |
| 44 | 1 | 0 | -9.946040 | -0.050873 | -0.000589 |
| 45 | 1 | 0 | -8.836608 | -2.071941 | -0.933145 |
| 46 | 1 | 0 | -6.381577 | -2.253761 | -0.924688 |
| 47 | 1 | 0 | -0.061808 | -1.770930 | 0.202707 |

E(RB+HF-LYP) = -1144.78923857 A.U. after 8 cycles
Zero-point correction= 0.373059 (Hartree/Particle)

**TS3:**

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -4.826322 | -2.098851 | 1.035244 |
| 2 | 6 | 0 | -4.777813 | -1.077830 | 0.069255 |
| 3 | 6 | 0 | -5.798761 | -1.013605 | -0.895906 |
| 4 | 6 | 0 | -6.838046 | -1.940570 | -0.892160 |
| 5 | 6 | 0 | -6.872297 | -2.951940 | 0.070371 |
| 6 | 6 | 0 | -5.862887 | -3.029084 | 1.032414 |
| 7 | 6 | 0 | -3.675862 | -0.091274 | 0.066856 |
| 8 | 6 | 0 | -3.105765 | 0.365709 | 1.272938 |
| 9 | 6 | 0 | -2.075572 | 1.297993 | 1.284876 |
| 10 | 6 | 0 | -1.592134 | 1.768394 | 0.064692 |
| 11 | 6 | 0 | -2.116054 | 1.336368 | -1.153708 |
| 12 | 6 | 0 | -3.159683 | 0.417873 | -1.141086 |
| 13 | 7 | 0 | -0.518453 | 2.749479 | 0.089734 |
| 14 | 7 | 0 | -0.551531 | 3.702949 | -0.809648 |
| 15 | 7 | 0 | -0.488747 | 4.602259 | -1.489422 |
| 16 | 7 | 0 | 0.642935 | 2.725636 | 0.798536 |
| 17 | 6 | 0 | 1.658559 | 1.753180 | 0.555330 |
| 18 | 6 | 0 | 1.656337 | 0.943333 | -0.580565 |
| 19 | 6 | 0 | 2.694886 | 0.035036 | -0.770749 |
| 20 | 6 | 0 | 3.748306 | -0.089002 | 0.150741 |
| 21 | 6 | 0 | 3.720787 | 0.745965 | 1.283020 |
| 22 | 6 | 0 | 2.695857 | 1.661988 | 1.488064 |
| 23 | 6 | 0 | 4.848535 | -1.058457 | -0.064478 |
| 24 | 6 | 0 | 6.169416 | -0.737286 | 0.292664 |
| 25 | 6 | 0 | 7.203863 | -1.647873 | 0.087153 |
| 26 | 6 | 0 | 6.937970 | -2.897481 | -0.476244 |
| 27 | 6 | 0 | 5.630000 | -3.230103 | -0.834186 |
| 28 | 6 | 0 | 4.595225 | -2.319223 | -0.631800 |

| | | | | | |
|---|---|---|---|---|---|
| 29 | 1 | 0 | -7.681565 | -3.676059 | 0.070946 |
| 30 | 1 | 0 | -5.878656 | -3.819102 | 1.777322 |
| 31 | 1 | 0 | -4.031159 | -2.187820 | 1.770116 |
| 32 | 1 | 0 | -7.625769 | -1.868892 | -1.636220 |
| 33 | 1 | 0 | -3.502075 | 0.012370 | 2.218818 |
| 34 | 1 | 0 | -1.664419 | 1.653694 | 2.224096 |
| 35 | 1 | 0 | -1.709338 | 1.687485 | -2.098622 |
| 36 | 1 | 0 | 0.586696 | 3.186239 | 1.699350 |
| 37 | 1 | 0 | 0.865641 | 1.011578 | -1.320513 |
| 38 | 1 | 0 | 2.697636 | -0.572342 | -1.670089 |
| 39 | 1 | 0 | 2.700144 | 2.292191 | 2.374358 |
| 40 | 1 | 0 | 3.577262 | -2.600824 | -0.887241 |
| 41 | 1 | 0 | 5.413316 | -4.203815 | -1.264134 |
| 42 | 1 | 0 | 7.744582 | -3.607179 | -0.635107 |
| 43 | 1 | 0 | 8.220055 | -1.377743 | 0.359591 |
| 44 | 1 | 0 | 6.394051 | 0.242923 | 0.704091 |
| 45 | 1 | 0 | 4.504168 | 0.662704 | 2.029371 |
| 46 | 1 | 0 | -5.799976 | -0.213811 | -1.631157 |
| 47 | 1 | 0 | -3.551300 | 0.056580 | -2.085809 |

E(UB+HF-LYP) = -1144.64756298 A.U. after 7 cycles
Zero-point correction= 0.373213 (Hartree/Particle)

**PC3a:**

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -4.297340 | -2.844497 | 0.251297 |
| 2 | 6 | 0 | -4.613083 | -1.492695 | 0.018957 |
| 3 | 6 | 0 | -5.959480 | -1.146686 | -0.201956 |
| 4 | 6 | 0 | -6.955139 | -2.119612 | -0.187509 |
| 5 | 6 | 0 | -6.625793 | -3.457911 | 0.039570 |
| 6 | 6 | 0 | -5.293589 | -3.817000 | 0.256852 |
| 7 | 6 | 0 | -3.555929 | -0.461417 | 0.007677 |
| 8 | 6 | 0 | -2.418383 | -0.573490 | 0.838734 |
| 9 | 6 | 0 | -1.413744 | 0.381164 | 0.834599 |
| 10 | 6 | 0 | -1.529060 | 1.493453 | -0.013224 |
| 11 | 6 | 0 | -2.664469 | 1.650932 | -0.821642 |
| 12 | 6 | 0 | -3.651120 | 0.675737 | -0.819811 |
| 13 | 7 | 0 | -0.605436 | 2.578226 | 0.017052 |
| 14 | 7 | 0 | 0.659536 | 2.686896 | 0.199229 |
| 15 | 7 | 0 | -1.941739 | 6.672773 | 0.005726 |
| 16 | 7 | 0 | -1.685859 | 5.599638 | -0.045753 |
| 17 | 6 | 0 | 1.583835 | 1.681985 | 0.148745 |

| | | | | | |
|---|---|---|---|---|---|
| 18 | 6 | 0 | 1.450463 | 0.369782 | -0.389619 |
| 19 | 6 | 0 | 2.551854 | -0.452547 | -0.466477 |
| 20 | 6 | 0 | 3.831141 | -0.051480 | 0.009536 |
| 21 | 6 | 0 | 3.954521 | 1.254398 | 0.537575 |
| 22 | 6 | 0 | 2.870744 | 2.105247 | 0.583341 |
| 23 | 6 | 0 | 4.982230 | -0.959874 | -0.062491 |
| 24 | 6 | 0 | 4.804506 | -2.358317 | -0.003318 |
| 25 | 6 | 0 | 5.897167 | -3.216482 | -0.058954 |
| 26 | 6 | 0 | 7.188903 | -2.699676 | -0.192861 |
| 27 | 6 | 0 | 7.382413 | -1.317108 | -0.262448 |
| 28 | 6 | 0 | 6.293770 | -0.455284 | -0.190025 |
| 29 | 1 | 0 | 8.040744 | -3.371261 | -0.243548 |
| 30 | 1 | 0 | 5.743553 | -4.289312 | 0.006444 |
| 31 | 1 | 0 | 3.810569 | -2.774110 | 0.129608 |
| 32 | 1 | 0 | 8.382955 | -0.911952 | -0.378712 |
| 33 | 1 | 0 | 2.444301 | -1.424634 | -0.935035 |
| 34 | 1 | 0 | 0.506207 | 0.025434 | -0.789987 |
| 35 | 1 | 0 | 2.967052 | 3.114526 | 0.969546 |
| 36 | 1 | 0 | -1.041111 | 3.501205 | -0.039055 |
| 37 | 1 | 0 | -0.572917 | 0.286970 | 1.512857 |
| 38 | 1 | 0 | -2.345530 | -1.404956 | 1.531642 |
| 39 | 1 | 0 | -2.755742 | 2.518007 | -1.470497 |
| 40 | 1 | 0 | -3.262390 | -3.142295 | 0.393091 |
| 41 | 1 | 0 | -5.029706 | -4.857016 | 0.424472 |
| 42 | 1 | 0 | -7.402894 | -4.216424 | 0.047834 |
| 43 | 1 | 0 | -7.990276 | -1.832206 | -0.346087 |
| 44 | 1 | 0 | -6.234658 | -0.106385 | -0.348933 |
| 45 | 1 | 0 | -4.499611 | 0.784975 | -1.486441 |
| 46 | 1 | 0 | 6.458052 | 0.614206 | -0.275532 |
| 47 | 1 | 0 | 4.909371 | 1.590774 | 0.925254 |

E(UB+HF-LYP) = -1144.77618221 A.U. after 4 cycles
Zero-point correction= 0.373877 (Hartree/Particle)

**PC3b:**

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 3.999872 | -2.168848 | -0.780283 |
| 2 | 6 | 0 | 4.354537 | -0.996098 | -0.090024 |
| 3 | 6 | 0 | 5.667225 | -0.894637 | 0.403884 |
| 4 | 6 | 0 | 6.587398 | -1.924900 | 0.217430 |
| 5 | 6 | 0 | 6.219274 | -3.082156 | -0.471357 |
| 6 | 6 | 0 | 4.920492 | -3.197989 | -0.970341 |

| | | | | | |
|---|---|---|---|---|---|
| 7 | 6 | 0 | 3.372866 | 0.097059 | 0.110993 |
| 8 | 6 | 0 | 2.424230 | 0.416379 | -0.876589 |
| 9 | 6 | 0 | 1.490219 | 1.430747 | -0.696893 |
| 10 | 6 | 0 | 1.474938 | 2.173371 | 0.501024 |
| 11 | 6 | 0 | 2.442426 | 1.885274 | 1.481543 |
| 12 | 6 | 0 | 3.361387 | 0.862271 | 1.292256 |
| 13 | 7 | 0 | 0.622316 | 3.254956 | 0.764240 |
| 14 | 7 | 0 | -0.518278 | 3.275350 | 0.125383 |
| 15 | 6 | 0 | -1.437803 | 2.119702 | 0.045195 |
| 16 | 6 | 0 | -1.440997 | 1.213950 | 1.106327 |
| 17 | 6 | 0 | -2.372528 | 0.180306 | 1.116514 |
| 18 | 6 | 0 | -3.318551 | 0.039987 | 0.087152 |
| 19 | 6 | 0 | -3.296189 | 0.978847 | -0.957980 |
| 20 | 6 | 0 | -2.367939 | 2.017052 | -0.987160 |
| 21 | 6 | 0 | -4.311015 | -1.064000 | 0.104536 |
| 22 | 6 | 0 | -5.630107 | -0.854412 | -0.331960 |
| 23 | 6 | 0 | -6.562412 | -1.890507 | -0.315228 |
| 24 | 6 | 0 | -6.195445 | -3.158959 | 0.137976 |
| 25 | 6 | 0 | -4.888211 | -3.382116 | 0.574208 |
| 26 | 6 | 0 | -3.956140 | -2.345716 | 0.557967 |
| 27 | 8 | 0 | -0.472850 | 3.822822 | -1.615868 |
| 28 | 1 | 0 | 6.936935 | -3.884841 | -0.618123 |
| 29 | 1 | 0 | 4.618877 | -4.097219 | -1.501486 |
| 30 | 1 | 0 | 2.984072 | -2.283634 | -1.148255 |
| 31 | 1 | 0 | 7.598298 | -1.818333 | 0.602663 |
| 32 | 1 | 0 | 2.438863 | -0.119726 | -1.821686 |
| 33 | 1 | 0 | 0.802433 | 1.693199 | -1.493584 |
| 34 | 1 | 0 | 2.443585 | 2.470401 | 2.396674 |
| 35 | 1 | 0 | -1.025141 | 4.126243 | 0.352825 |
| 36 | 1 | 0 | -0.728872 | 1.320854 | 1.915973 |
| 37 | 1 | 0 | -2.384184 | -0.510317 | 1.954271 |
| 38 | 1 | 0 | -2.333199 | 2.721534 | -1.806889 |
| 39 | 1 | 0 | -2.934392 | -2.537294 | 0.873780 |
| 40 | 1 | 0 | -4.589745 | -4.368053 | 0.920471 |
| 41 | 1 | 0 | -6.921971 | -3.966798 | 0.150795 |
| 42 | 1 | 0 | -7.579552 | -1.703954 | -0.649425 |
| 43 | 1 | 0 | -5.933102 | 0.135366 | -0.662094 |
| 44 | 1 | 0 | -3.997529 | 0.878988 | -1.781002 |
| 45 | 1 | 0 | 5.976125 | 0.012884 | 0.915080 |
| 46 | 1 | 0 | 4.070160 | 0.634741 | 2.083677 |
| 47 | 1 | 0 | 0.387725 | 4.273601 | -1.539250 |

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E(UB+HF-LYP) = -1111.20747392 A.U. after 4 cycles
Zero-point correction= 0.380159 (Hartree/Particle)

**TS4:**

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -5.562982 | -0.896928 | -0.348490 |
| 2 | 6 | 0 | -4.249657 | -1.096387 | 0.110325 |
| 3 | 6 | 0 | -3.892418 | -2.376654 | 0.566791 |
| 4 | 6 | 0 | -4.815882 | -3.420718 | 0.564553 |
| 5 | 6 | 0 | -6.117220 | -3.207301 | 0.106273 |
| 6 | 6 | 0 | -6.486678 | -1.940715 | -0.350227 |
| 7 | 6 | 0 | -3.267099 | 0.015658 | 0.112171 |
| 8 | 6 | 0 | -2.329647 | 0.153213 | 1.151267 |
| 9 | 6 | 0 | -1.407777 | 1.193232 | 1.158875 |
| 10 | 6 | 0 | -1.405583 | 2.118165 | 0.108678 |
| 11 | 6 | 0 | -2.324606 | 2.012000 | -0.936232 |
| 12 | 6 | 0 | -3.242405 | 0.965289 | -0.923696 |
| 13 | 7 | 0 | -0.521162 | 3.264315 | 0.213656 |
| 14 | 7 | 0 | 0.646333 | 3.291991 | 0.749878 |
| 15 | 6 | 0 | 1.481662 | 2.186437 | 0.528828 |
| 16 | 6 | 0 | 1.479069 | 1.462396 | -0.679561 |
| 17 | 6 | 0 | 2.402085 | 0.443975 | -0.876365 |
| 18 | 6 | 0 | 3.345026 | 0.101194 | 0.111409 |
| 19 | 6 | 0 | 3.348060 | 0.851692 | 1.302187 |
| 20 | 6 | 0 | 2.448105 | 1.890164 | 1.503677 |
| 21 | 6 | 0 | 4.311320 | -1.002980 | -0.103330 |
| 22 | 6 | 0 | 5.626593 | -0.922607 | 0.387010 |
| 23 | 6 | 0 | 6.531904 | -1.963137 | 0.186303 |
| 24 | 6 | 0 | 6.144237 | -3.108825 | -0.511067 |
| 25 | 6 | 0 | 4.842059 | -3.203408 | -1.005610 |
| 26 | 6 | 0 | 3.936633 | -2.163265 | -0.803560 |
| 27 | 8 | 0 | -0.697947 | 4.091201 | -1.695832 |
| 28 | 1 | 0 | 6.850263 | -3.919696 | -0.668231 |
| 29 | 1 | 0 | 4.526361 | -4.093678 | -1.543264 |
| 30 | 1 | 0 | 2.918161 | -2.260493 | -1.169065 |
| 31 | 1 | 0 | 7.545852 | -1.874005 | 0.567459 |
| 32 | 1 | 0 | 2.415161 | -0.077535 | -1.829146 |
| 33 | 1 | 0 | 0.791045 | 1.754226 | -1.467132 |
| 34 | 1 | 0 | 2.463695 | 2.471241 | 2.420984 |
| 35 | 1 | 0 | -0.963691 | 4.179870 | 0.092046 |
| 36 | 1 | 0 | -0.709705 | 1.298645 | 1.981645 |
| 37 | 1 | 0 | -2.344914 | -0.543489 | 1.983915 |
| 38 | 1 | 0 | -2.260645 | 2.719787 | -1.753009 |
| 39 | 1 | 0 | -2.874734 | -2.561070 | 0.899562 |
| 40 | 1 | 0 | -4.515314 | -4.405045 | 0.913647 |
| 41 | 1 | 0 | -6.837202 | -4.021082 | 0.104691 |
| 42 | 1 | 0 | -7.499402 | -1.761631 | -0.701447 |

| | | | | | |
|---|---|---|---|---|---|
| 43 | 1 | 0 | -5.868595 | 0.091089 | -0.681181 |
| 44 | 1 | 0 | -3.932042 | 0.864240 | -1.756460 |
| 45 | 1 | 0 | 5.950002 | -0.024204 | 0.905193 |
| 46 | 1 | 0 | 4.056525 | 0.604775 | 2.087511 |
| 47 | 1 | 0 | 0.227755 | 4.391362 | -1.727041 |

E(UB+HF-LYP) = -1111.20472123 A.U. after 9 cycles
Zero-point correction= 0.377671 (Hartree/Particle)

**PC4:**

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 4.158251 | -2.145595 | -0.576029 |
| 2 | 6 | 0 | 4.481272 | -0.855147 | -0.122008 |
| 3 | 6 | 0 | 5.822408 | -0.581148 | 0.197466 |
| 4 | 6 | 0 | 6.804365 | -1.561916 | 0.068587 |
| 5 | 6 | 0 | 6.467770 | -2.839366 | -0.383034 |
| 6 | 6 | 0 | 5.139986 | -3.126572 | -0.704909 |
| 7 | 6 | 0 | 3.434455 | 0.186976 | 0.017344 |
| 8 | 6 | 0 | 2.382360 | 0.288436 | -0.911881 |
| 9 | 6 | 0 | 1.386275 | 1.248362 | -0.779123 |
| 10 | 6 | 0 | 1.428445 | 2.157340 | 0.289769 |
| 11 | 6 | 0 | 2.500689 | 2.107083 | 1.190569 |
| 12 | 6 | 0 | 3.468824 | 1.116245 | 1.072312 |
| 13 | 7 | 0 | 0.544978 | 3.275507 | 0.401256 |
| 14 | 7 | 0 | -0.698981 | 3.205626 | 0.269712 |
| 15 | 6 | 0 | -1.457110 | 1.992032 | 0.212147 |
| 16 | 6 | 0 | -1.234392 | 0.886323 | 1.048512 |
| 17 | 6 | 0 | -2.112819 | -0.189267 | 1.017643 |
| 18 | 6 | 0 | -3.219943 | -0.209675 | 0.147784 |
| 19 | 6 | 0 | -3.437380 | 0.916841 | -0.665012 |
| 20 | 6 | 0 | -2.589606 | 2.017629 | -0.615064 |
| 21 | 6 | 0 | -4.136876 | -1.375295 | 0.107611 |
| 22 | 6 | 0 | -5.519315 | -1.203114 | -0.079899 |
| 23 | 6 | 0 | -6.378523 | -2.299815 | -0.119772 |
| 24 | 6 | 0 | -5.875288 | -3.593907 | 0.026583 |
| 25 | 6 | 0 | -4.504541 | -3.781030 | 0.213943 |
| 26 | 6 | 0 | -3.645542 | -2.684183 | 0.254289 |
| 27 | 8 | 0 | -2.320999 | 5.289364 | -1.031519 |
| 28 | 1 | 0 | 7.233255 | -3.603885 | -0.483695 |
| 29 | 1 | 0 | 4.865217 | -4.119930 | -1.049765 |
| 30 | 1 | 0 | 3.124105 | -2.388415 | -0.804243 |
| 31 | 1 | 0 | 7.836320 | -1.324448 | 0.313172 |
| 32 | 1 | 0 | 2.358448 | -0.382505 | -1.765695 |

| | | | | | |
|---|---|---|---|---|---|
| 33 | 1 | 0 | 0.591016 | 1.311667 | -1.514509 |
| 34 | 1 | 0 | 2.549230 | 2.840678 | 1.989893 |
| 35 | 1 | 0 | -1.775324 | 4.801378 | -0.381856 |
| 36 | 1 | 0 | -0.398050 | 0.881609 | 1.738715 |
| 37 | 1 | 0 | -1.954559 | -1.020456 | 1.698538 |
| 38 | 1 | 0 | -2.783890 | 2.909089 | -1.205453 |
| 39 | 1 | 0 | -2.577485 | -2.843786 | 0.373926 |
| 40 | 1 | 0 | -4.100719 | -4.784380 | 0.320954 |
| 41 | 1 | 0 | -6.545389 | -4.448678 | -0.004580 |
| 42 | 1 | 0 | -7.444988 | -2.141841 | -0.256831 |
| 43 | 1 | 0 | -5.926365 | -0.199755 | -0.167339 |
| 44 | 1 | 0 | -4.281386 | 0.930048 | -1.348185 |
| 45 | 1 | 0 | 6.101230 | 0.417175 | 0.523033 |
| 46 | 1 | 0 | 4.262434 | 1.058199 | 1.811444 |
| 47 | 1 | 0 | -1.669683 | 5.597962 | -1.679114 |

E(UB+HF-LYP) = -1111.27539485 A.U. after 1 cycles
Zero-point correction= 0.377453 (Hartree/Particle)

***Cis* azo**

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -4.306511 | -0.823084 | -0.056642 |
| 2 | 6 | 0 | -4.773125 | -1.336015 | -1.279367 |
| 3 | 6 | 0 | -5.701500 | -2.375154 | -1.313119 |
| 4 | 6 | 0 | -6.185381 | -2.925221 | -0.124686 |
| 5 | 6 | 0 | -5.731588 | -2.426468 | 1.097802 |
| 6 | 6 | 0 | -4.802762 | -1.387781 | 1.131165 |
| 7 | 1 | 0 | -4.426337 | -0.896430 | -2.210380 |
| 8 | 1 | 0 | -6.054608 | -2.749348 | -2.270478 |
| 9 | 1 | 0 | -6.909538 | -3.734893 | -0.150935 |
| 10 | 1 | 0 | -6.094964 | -2.852732 | 2.029210 |
| 11 | 1 | 0 | -4.436503 | -1.026089 | 2.088009 |
| 12 | 6 | 0 | -3.319700 | 0.283930 | -0.018445 |
| 13 | 6 | 0 | -3.398769 | 1.291887 | 0.959506 |
| 14 | 6 | 0 | -2.490187 | 2.343553 | 0.982262 |
| 15 | 6 | 0 | -1.433988 | 2.386575 | 0.061869 |
| 16 | 6 | 0 | -1.349101 | 1.397917 | -0.930223 |
| 17 | 6 | 0 | -2.285933 | 0.371208 | -0.968401 |
| 18 | 1 | 0 | -4.211763 | 1.275664 | 1.679579 |
| 19 | 1 | 0 | -2.584814 | 3.146509 | 1.707379 |
| 20 | 1 | 0 | -0.557750 | 1.438405 | -1.671086 |

| | | | | | |
|---|---|---|---|---|---|
| 21 | 1 | 0 | -2.197981 | -0.395498 | -1.732887 |
| 22 | 7 | 0 | -0.620608 | 3.565225 | 0.075769 |
| 23 | 7 | 0 | 0.620892 | 3.565732 | -0.077649 |
| 24 | 6 | 0 | 1.434712 | 2.387813 | -0.066139 |
| 25 | 6 | 0 | 2.485090 | 2.337956 | -0.992553 |
| 26 | 6 | 0 | 3.393154 | 1.285753 | -0.967528 |
| 27 | 6 | 0 | 3.319443 | 0.284485 | 0.017629 |
| 28 | 6 | 0 | 2.290984 | 0.378521 | 0.972713 |
| 29 | 6 | 0 | 1.354843 | 1.405692 | 0.932968 |
| 30 | 1 | 0 | 2.576145 | 3.135338 | -1.724245 |
| 31 | 1 | 0 | 4.202006 | 1.264332 | -1.692133 |
| 32 | 1 | 0 | 2.206441 | -0.383343 | 1.742384 |
| 33 | 1 | 0 | 0.567290 | 1.452289 | 1.677592 |
| 34 | 6 | 0 | 4.306304 | -0.822615 | 0.057677 |
| 35 | 6 | 0 | 4.780581 | -1.326607 | 1.281209 |
| 36 | 6 | 0 | 5.708917 | -2.365690 | 1.316853 |
| 37 | 6 | 0 | 6.185270 | -2.924664 | 0.129533 |
| 38 | 6 | 0 | 5.723947 | -2.434790 | -1.093725 |
| 39 | 6 | 0 | 4.795077 | -1.396218 | -1.128951 |
| 40 | 1 | 0 | 4.440158 | -0.879834 | 2.211128 |
| 41 | 1 | 0 | 6.068030 | -2.732796 | 2.274724 |
| 42 | 1 | 0 | 6.909481 | -3.734242 | 0.157231 |
| 43 | 1 | 0 | 6.081421 | -2.868016 | -2.024204 |
| 44 | 1 | 0 | 4.422641 | -1.041898 | -2.086171 |

E(UB+HF-LYP) = -1034.85335727 A.U. after 3 cycles
Zero-point correction= 0.352920 (Hartree/Particle)

***Trans* azo:**

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 6.692407 | -0.994059 | 0.736839 |
| 2 | 6 | 0 | 6.043478 | 0.014207 | 0.002717 |
| 3 | 6 | 0 | 6.836630 | 0.918335 | -0.725258 |
| 4 | 6 | 0 | 8.226724 | 0.817847 | -0.719683 |
| 5 | 6 | 0 | 8.856370 | -0.188874 | 0.014804 |
| 6 | 6 | 0 | 8.082515 | -1.094146 | 0.743337 |
| 7 | 6 | 0 | 4.564210 | 0.120721 | -0.002902 |
| 8 | 6 | 0 | 3.926467 | 1.373147 | -0.015022 |
| 9 | 6 | 0 | 2.539181 | 1.467350 | -0.018833 |
| 10 | 6 | 0 | 1.746549 | 0.311678 | -0.010465 |
| 11 | 6 | 0 | 2.370548 | -0.948544 | 0.000508 |
| 12 | 6 | 0 | 3.754300 | -1.034559 | 0.004106 |

| | | | | | |
|---|---|---|---|---|---|
| 13 | 7 | 0 | 0.348881 | 0.526576 | -0.012265 |
| 14 | 7 | 0 | -0.348880 | -0.526567 | -0.012263 |
| 15 | 6 | 0 | -1.746548 | -0.311670 | -0.010460 |
| 16 | 6 | 0 | -2.370551 | 0.948551 | 0.000514 |
| 17 | 6 | 0 | -3.754303 | 1.034562 | 0.004112 |
| 18 | 6 | 0 | -4.564210 | -0.120720 | -0.002897 |
| 19 | 6 | 0 | -3.926464 | -1.373145 | -0.015017 |
| 20 | 6 | 0 | -2.539178 | -1.467344 | -0.018828 |
| 21 | 6 | 0 | -6.043478 | -0.014209 | 0.002720 |
| 22 | 6 | 0 | -6.692412 | 0.994054 | 0.736842 |
| 23 | 6 | 0 | -8.082520 | 1.094138 | 0.743335 |
| 24 | 6 | 0 | -8.856371 | 0.188865 | 0.014799 |
| 25 | 6 | 0 | -8.226720 | -0.817853 | -0.719687 |
| 26 | 6 | 0 | -6.836626 | -0.918339 | -0.725258 |
| 27 | 1 | 0 | -1.751995 | 1.839033 | -0.003300 |
| 28 | 1 | 0 | -4.226576 | 2.012769 | -0.015201 |
| 29 | 1 | 0 | -4.524700 | -2.279267 | 0.007346 |
| 30 | 1 | 0 | -2.041273 | -2.432328 | -0.018068 |
| 31 | 1 | 0 | -6.102122 | 1.687258 | 1.329423 |
| 32 | 1 | 0 | -8.562289 | 1.876337 | 1.325769 |
| 33 | 1 | 0 | -9.940129 | 0.267262 | 0.019179 |
| 34 | 1 | 0 | -8.818854 | -1.522536 | -1.297652 |
| 35 | 1 | 0 | -6.356730 | -1.688485 | -1.322615 |
| 36 | 1 | 0 | 2.041278 | 2.432335 | -0.018072 |
| 37 | 1 | 0 | 4.524705 | 2.279268 | 0.007341 |
| 38 | 1 | 0 | 4.226570 | -2.012767 | -0.015207 |
| 39 | 1 | 0 | 1.751990 | -1.839025 | -0.003305 |
| 40 | 1 | 0 | 6.356737 | 1.688484 | -1.322615 |
| 41 | 1 | 0 | 8.818862 | 1.522529 | -1.297644 |
| 42 | 1 | 0 | 9.940128 | -0.267273 | 0.019187 |
| 43 | 1 | 0 | 8.562281 | -1.876347 | 1.325772 |
| 44 | 1 | 0 | 6.102113 | -1.687262 | 1.329418 |

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E(RB+HF-LYP) = -1034.87795492 A.U. after 6 cycles
Zero-point correction= 0.353352 (Hartree/Particle)