# Supporting Information

## 2-Pyridylnitrene, 3-Pyridazylcarbene and their Relationship via Ring Expansion, Ring Opening, Ring Contraction, and Fragmentation

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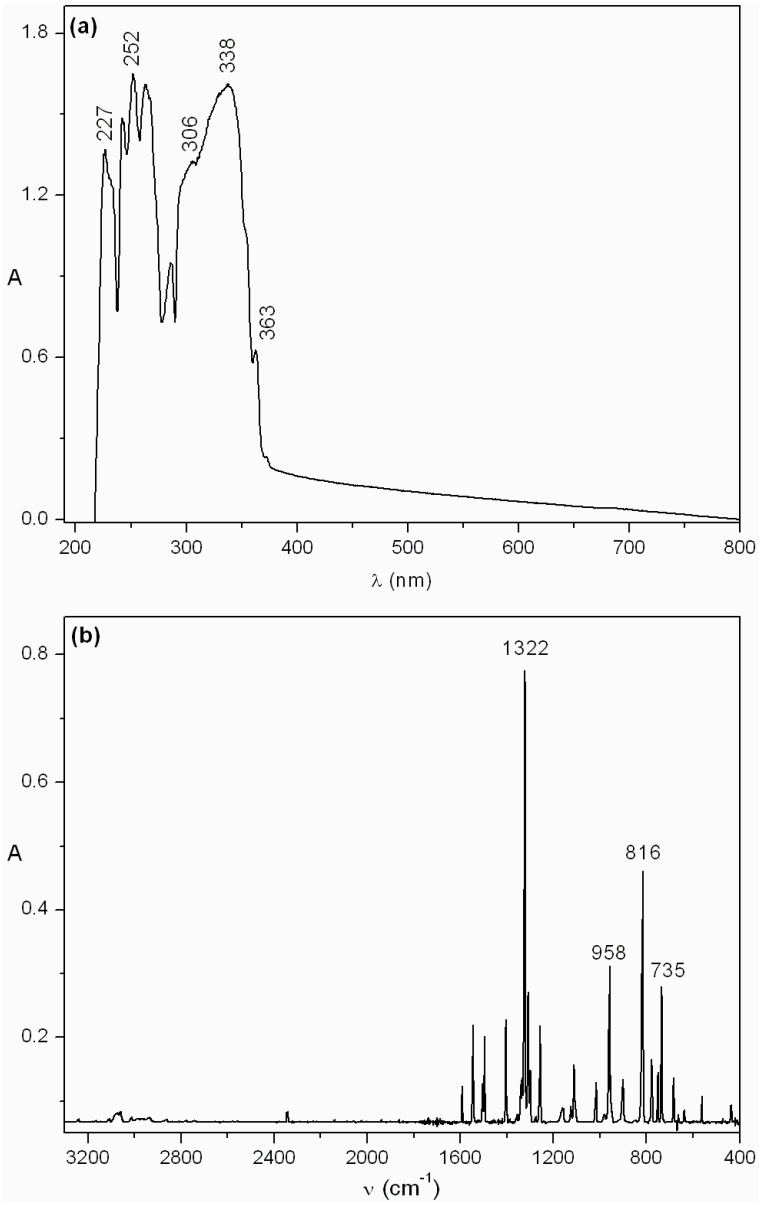



**Figure S1.** (a) UV spectrum of triazolo[1,5-*b*]pyridazine **8** in Ar matrix, and (b) the corresponding matrix IR spectrum, obtained by FVT of **8** at 200 ºC (8 x $10^{-6}$ mbar).

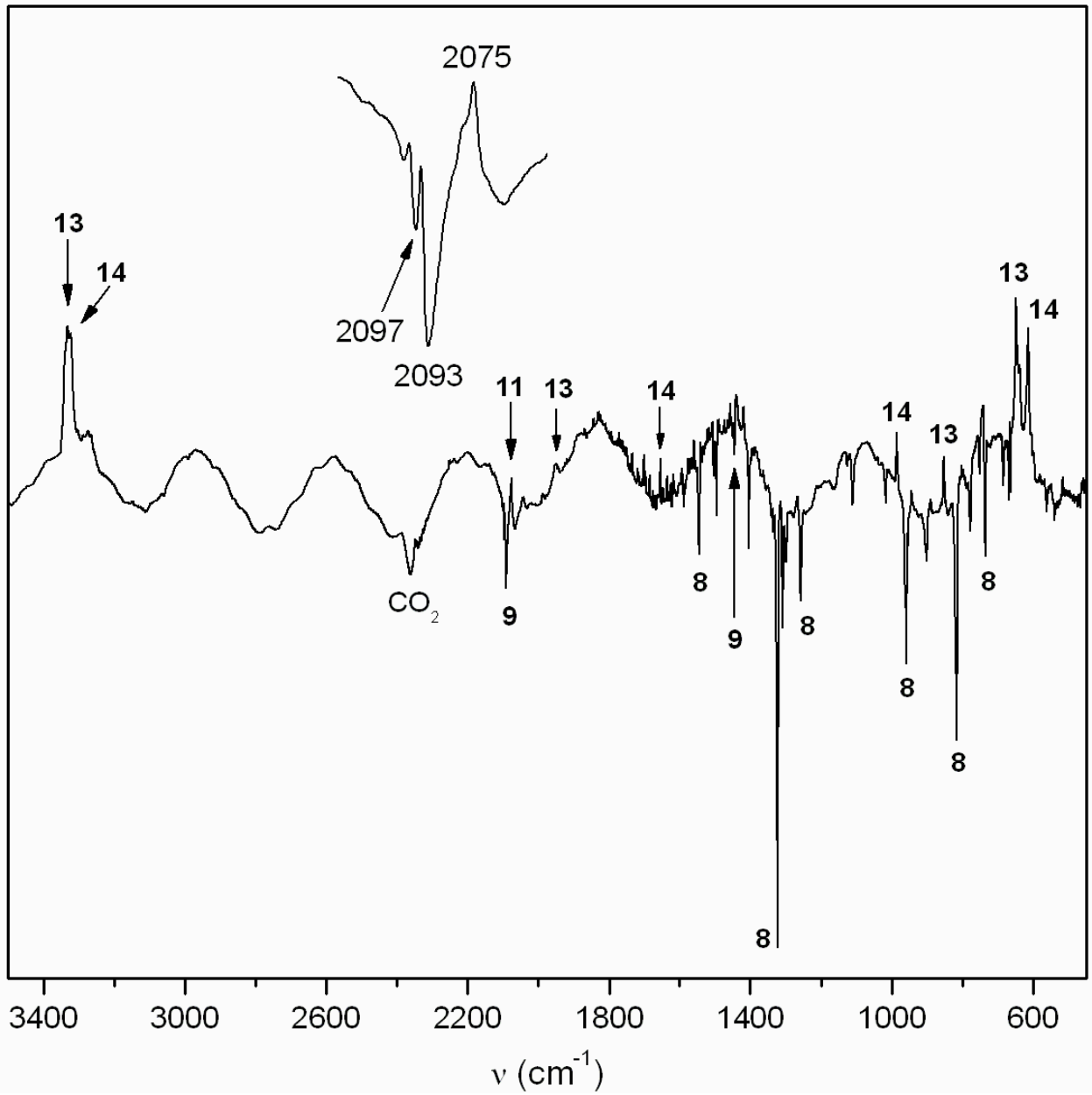



**Figure S2.** Difference IR spectrum showing a mixture of **11** as well as **13** and **14** (positive peaks), formed at the expense of triazole **8** and **9Z,E** (negative peaks), obtained by photolysis of **8** at 222 nm for 40 min. This spectrum is consistent with the order of photolysis **8** → **9** → **11** → **13**/**14**.

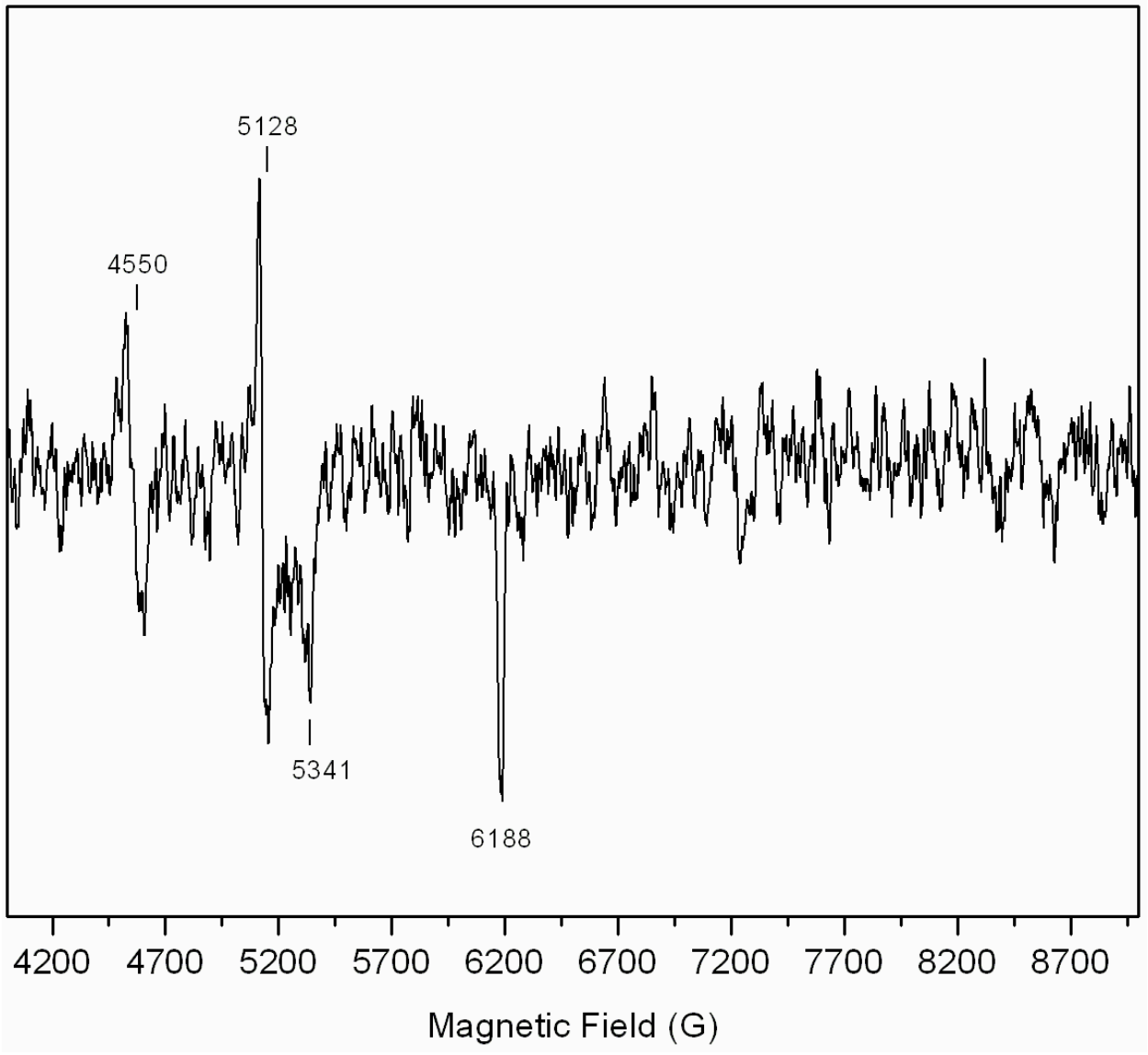



**Figure S3.** ESR spectrum obtained after 45 s of photolysis of **8** at 308 nm in Ar matrix (the spectrum is an early stage of the experiment described in Figure 3). The peaks are weak at short photolysis times, but the spectrum shows the presence of **10** (5128, 6188 G) and only one isomer of **12** (4550 ,5341 G)..

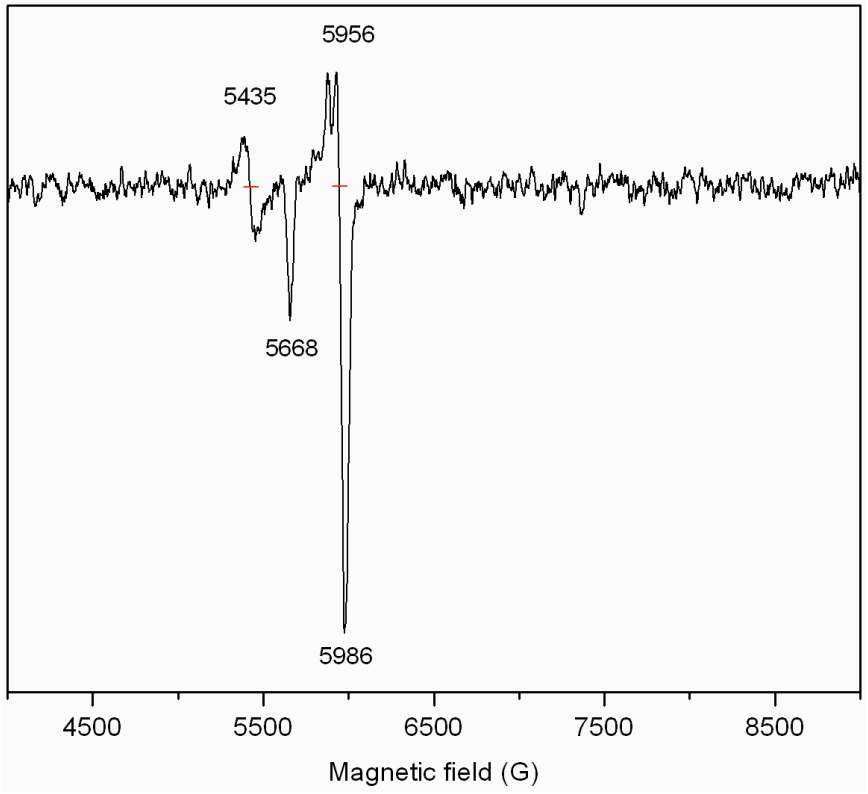
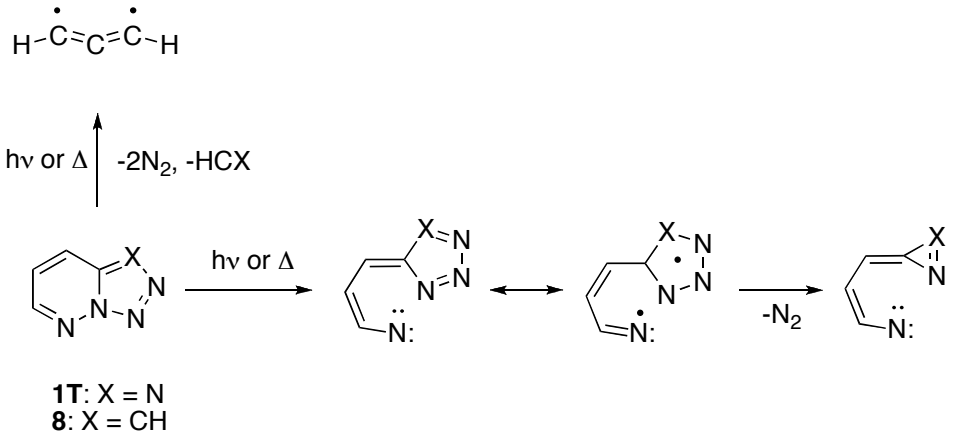



**Figure S4.** Difference ESR spectrum of unassigned triplet species after photolysis of **8** at 308 nm for 7 min (not shown) and 222 nm for 30 min. Ar matrix, 10-15 K.
Species **A**: $D/hc$ = 0.5057 ; $E/hc$ = 0.0057 $cm^{-1}$ (**A**: $X_2$ = 5435; $Y_2$ = 5668 G).
Species **B**: $D/hc$ = 0.6357; $E/hc$ = 0.0007 $cm^{-1}$ (**B**: $X_2$ = 5956; $Y_2$ = 5986 G). The apparent splitting of the $X_2$ signal is not always present.
Microwave frequency 9.7272 GHz, $H_0$= 3471 G.




**Scheme S1**. Potential carriers of the major triplet signal B ( $X_2$= 5956; $Y_2$ = 5986 G) in Figure S4, which is formed on matrix photolysis of **8** and either FVT or photolysis of **1T**.

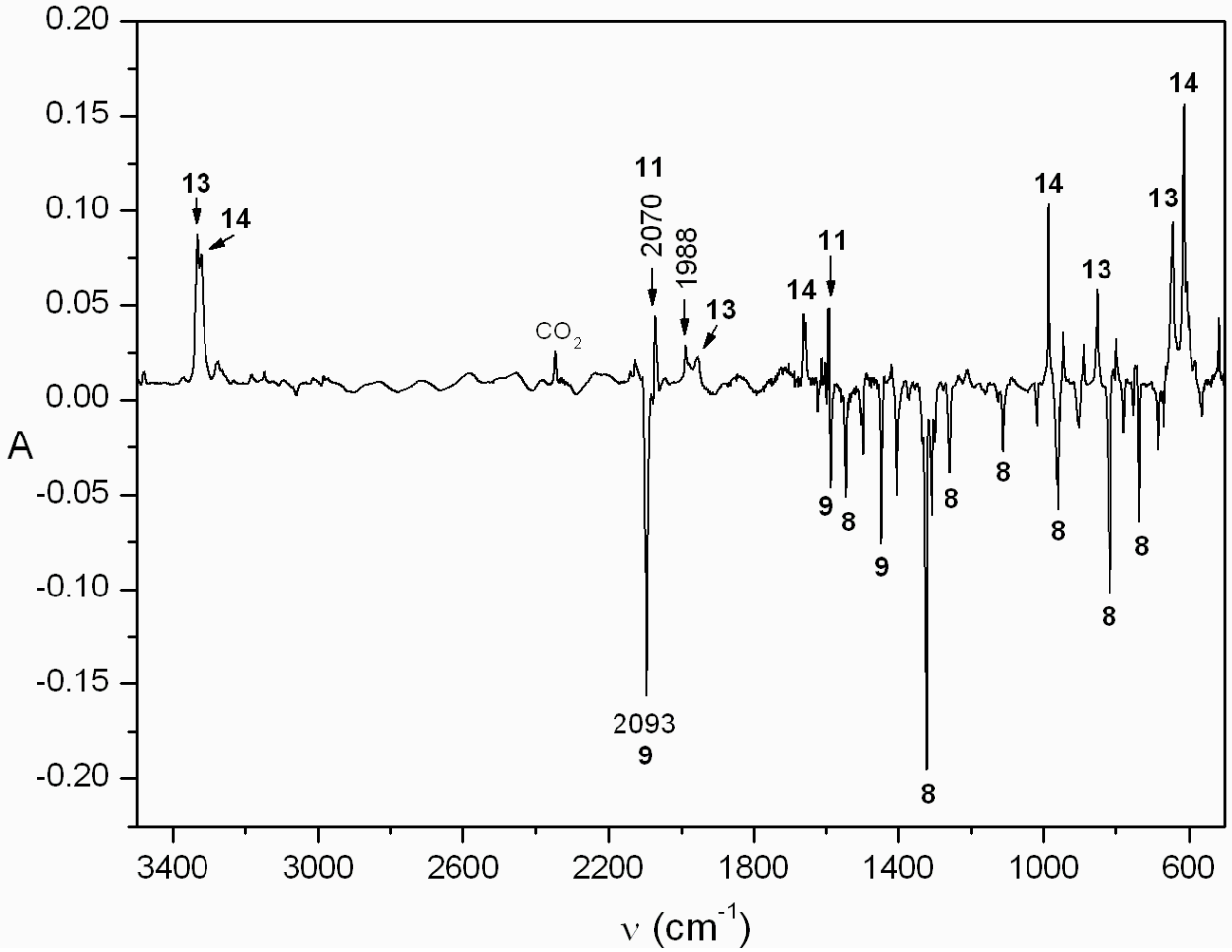



**Figure S5.** Ar matrix IR spectrum from prolonged photolysis of triazole **8** at 254 nm (low pressure Hg lamp). Positive peaks, a mixture of **11**, **13** and **14** after photolysis for 7 h. Negative peaks, a mixture of **9** and **8** after photoysis for 5 h. The positive peak at 1988 $cm^{-1}$ is possibly due to cyclic carbodiimide **21** (see text).

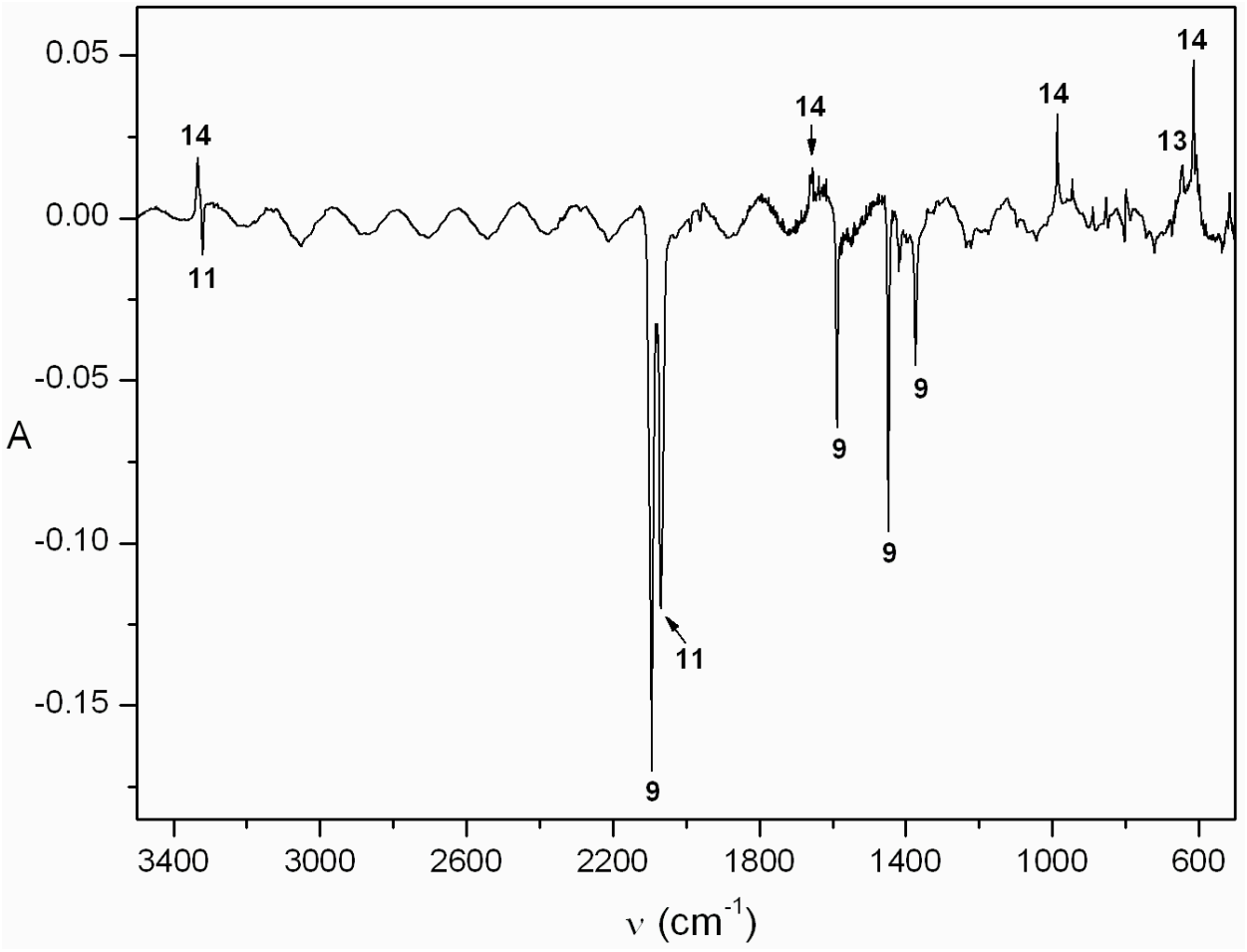



**Figure S6**. Matrix IR spectrum from photolysis of a mixture of diazo compounds **9** and **11** at 281 nm (interference filter) for 20 min (positive peaks, **14** and a trace of **13**), after initial photolysis of triazole **8** at 254 nm for 4 h (negative peaks, a mixture of **9** and **11**). The photolysis at 281 nm apparently does not touch the triazole **8** which has minimum absorption in the UV spectrum at 281 nm (Figure S1).

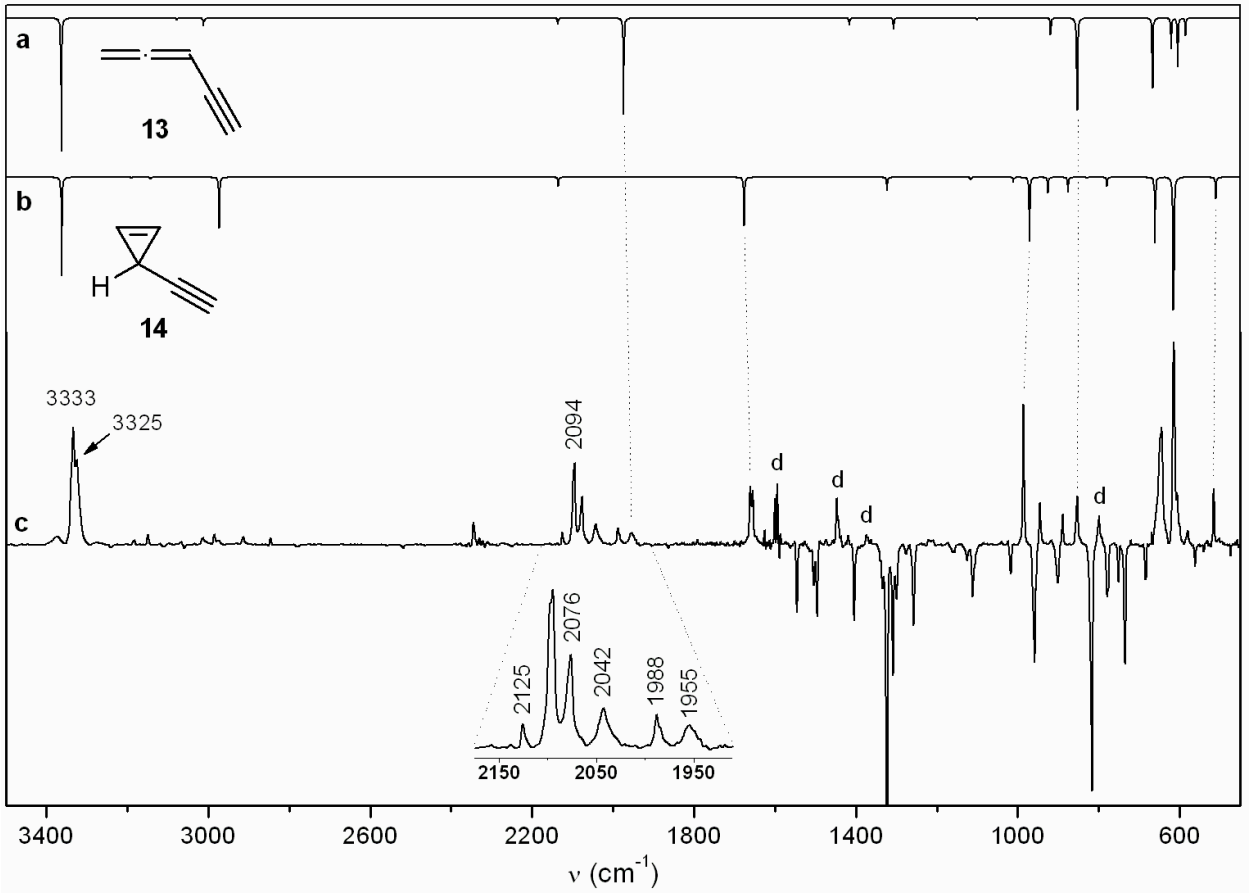



**Figure S7.** Matrix IR and calculated spectra of 1,2-pentadien-4-yne **13** and 3-ethynylcyclopropene **14**. (a) Calculated spectrum of **13**, and (b) calculated spectrum of **14** at the B3LYP/6-311G** level, wavenumbers scaled by 0.967. (c) Difference IR spectrum obtained after photolysis at 222 nm for 4 min, then > 405 nm for 45 min (not shown), and 308 nm for **13** min. The negative spectrum is due to triazole **8** before photolysis. Peaks belonging to the diazo compounds **9** (2094 $cm^{-1}$) are labeled "d". Diazo compound **11** appears at 2076 cm-1 (see also Figures 1 and 2). Allene **13** appears at 1955 $cm^{-1}$. The peak at 1988 $cm^{-1}$is possibly due to the cyclic carbodiimide **21**. The peak at 2042 $cm^{-1}$ is assigned to a ketenimine (see paper proper).

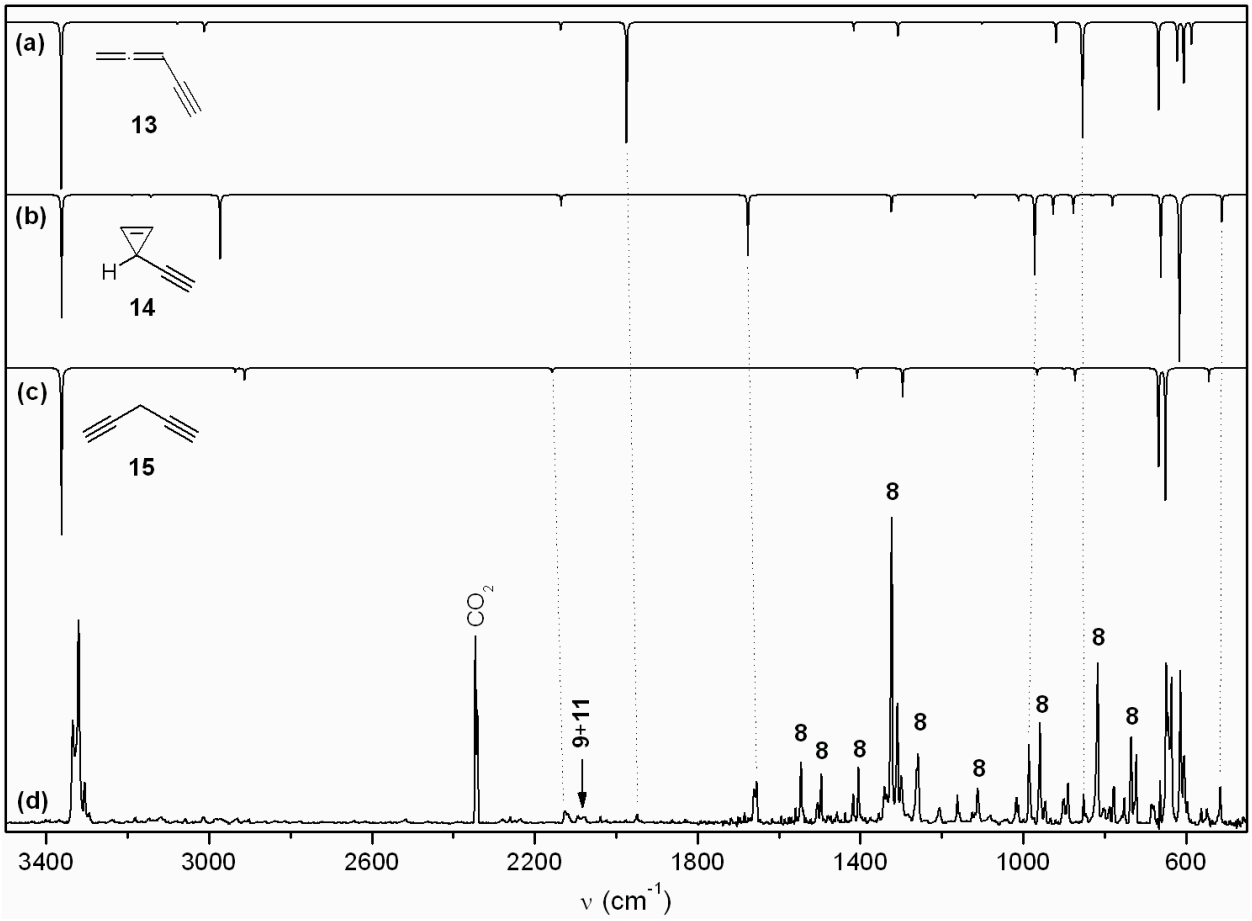



**Figure S8.** IR spectrum from the FVT of **8** at 600 °C, and calculated spectra showing absorptions of 1,4-pentadiyne **15**, 1,2-pentadien-4-yne **13**, and 3-ethynylcyclopropene **14**. (a) Calculated spectrum of **13**, (b) calculated spectrum of **14** and (c) calculated spectrum of 1,4-pentadiyne **15** at the B3LYP/6-311G** level, scaled by 0.967. (d) Product of FVT at 600 °C in Ar matrix, showing absorptions of **8**, **9**, **11**, **13**, **14**, and **15**. The presence of both diazo compounds, **9** and **11**, is indicated by the 2094-2071 bands.

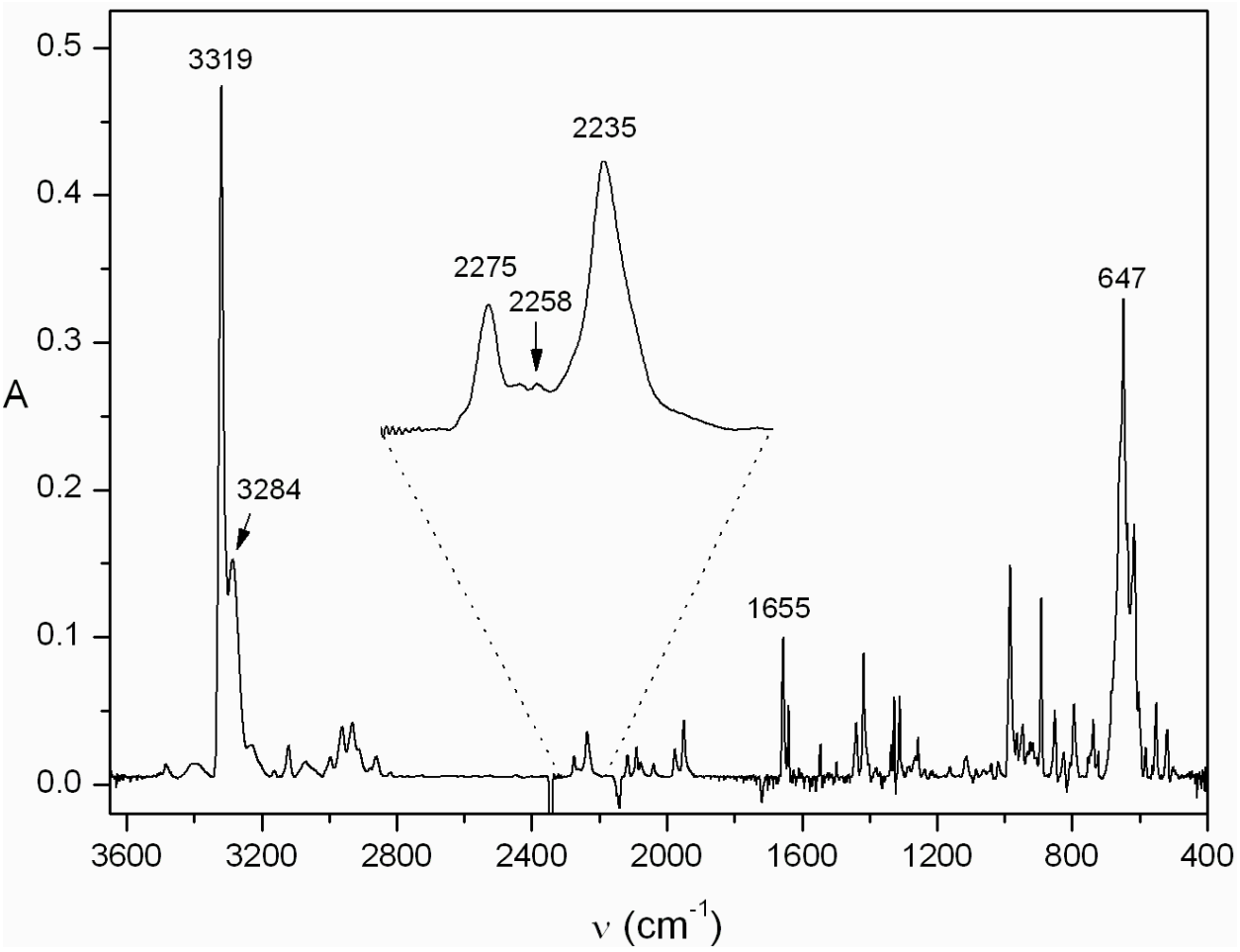



**Figure S9**. Ar matrix IR (difference) spectrum obtained from the FVT of **8** at 700 °C, showing CN peaks of glutacononitrile (2275 and 2235 $cm^{-1}$), 2-cyanopyrrole (2235 $cm^{-1}$), and 3-cyanopyrrole (2260 $cm^{-1}$). The absorption at 3284 $cm^{-1}$ is probably due to NH stretches in cyanopyrroles. The strong band at 3319-3333 $cm^{-1}$ is due to acetylenes **13-15**.

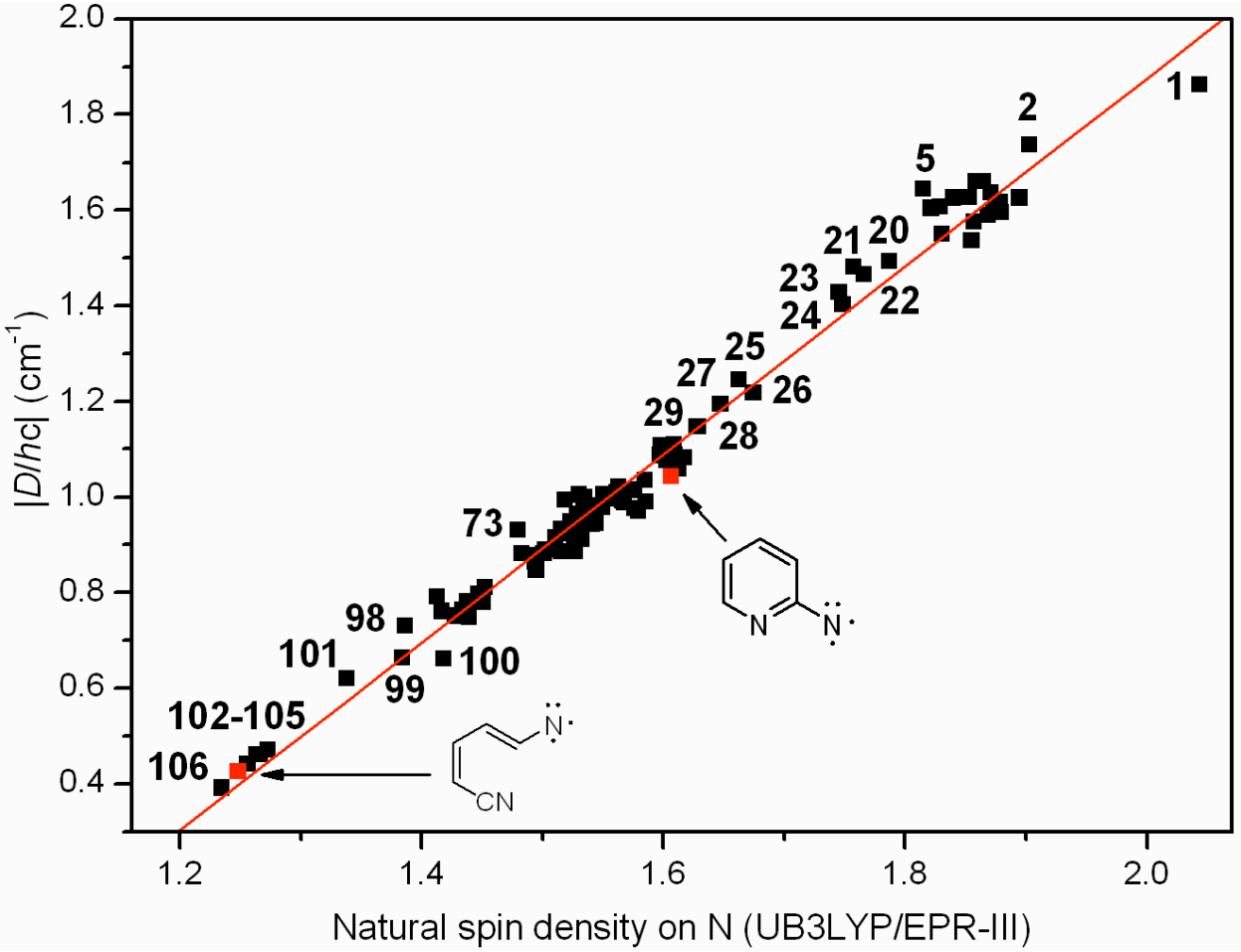



**Figure S10**. *D*-$\rho$ correlation with data point for nitrene **19** ($D$ = 1.0414 cm$^{-1}$, $\rho$ = 1.6068), and nitrene **23** ($D$ = 0.4253 cm$^{-1}$, $\rho$ = 1.2486) added. For more details and complete list of nitrenes, see ref. 6.

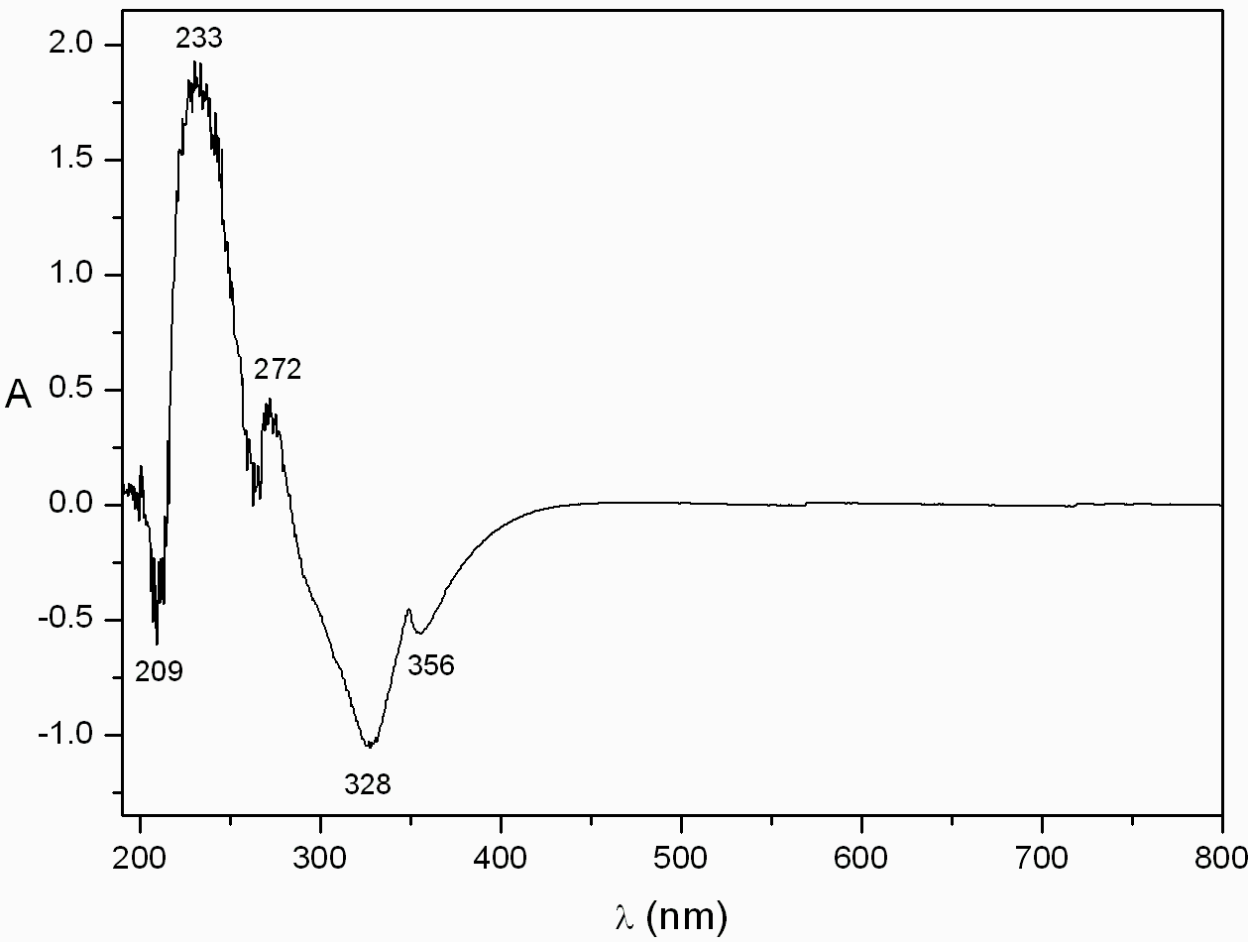



**Figure S11.** Difference UV spectrum obtained after photolysis of tetrazolopyridine **22T** in Ar matrix at 222 nm for 30 min (not shown), followed by 308 nm (30 min). Negative bands belong to diazacycloheptatetraene **21**. The product band at 233 and 272 nm are assigned to spiroazirene **25**, in relation to the corresponding matrix IR spectrum shown on Figure 7.

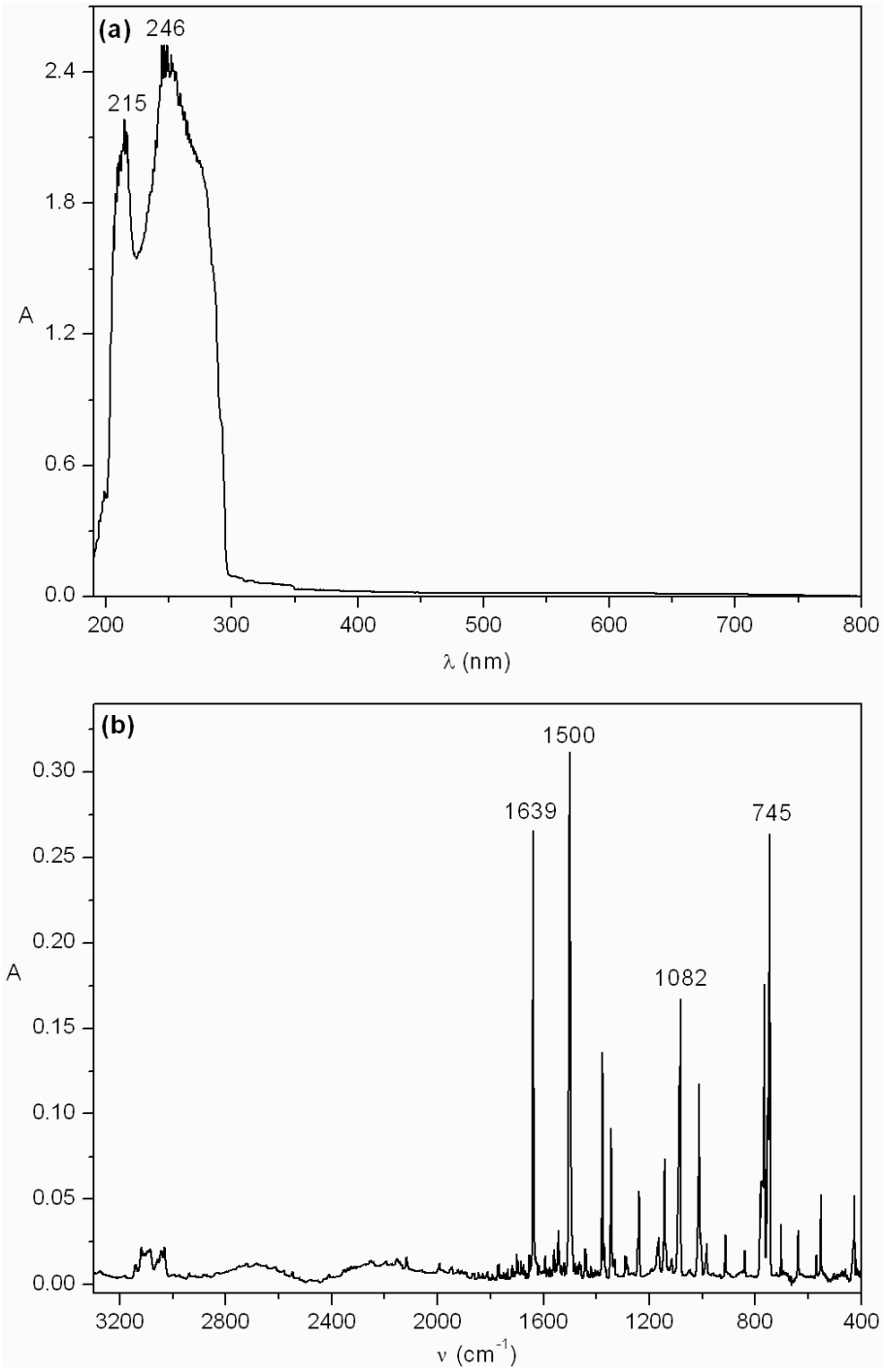



**Figure S12.** (a) Difference UV spectrum of tetrazolo[1,5-*a*]pyridine **22T** (Ar, 7K), and (b) its corresponding matrix IR spectrum, obtained from sublimation of **22T** at 80 ºC (8 x $10^{-6}$ mbar).

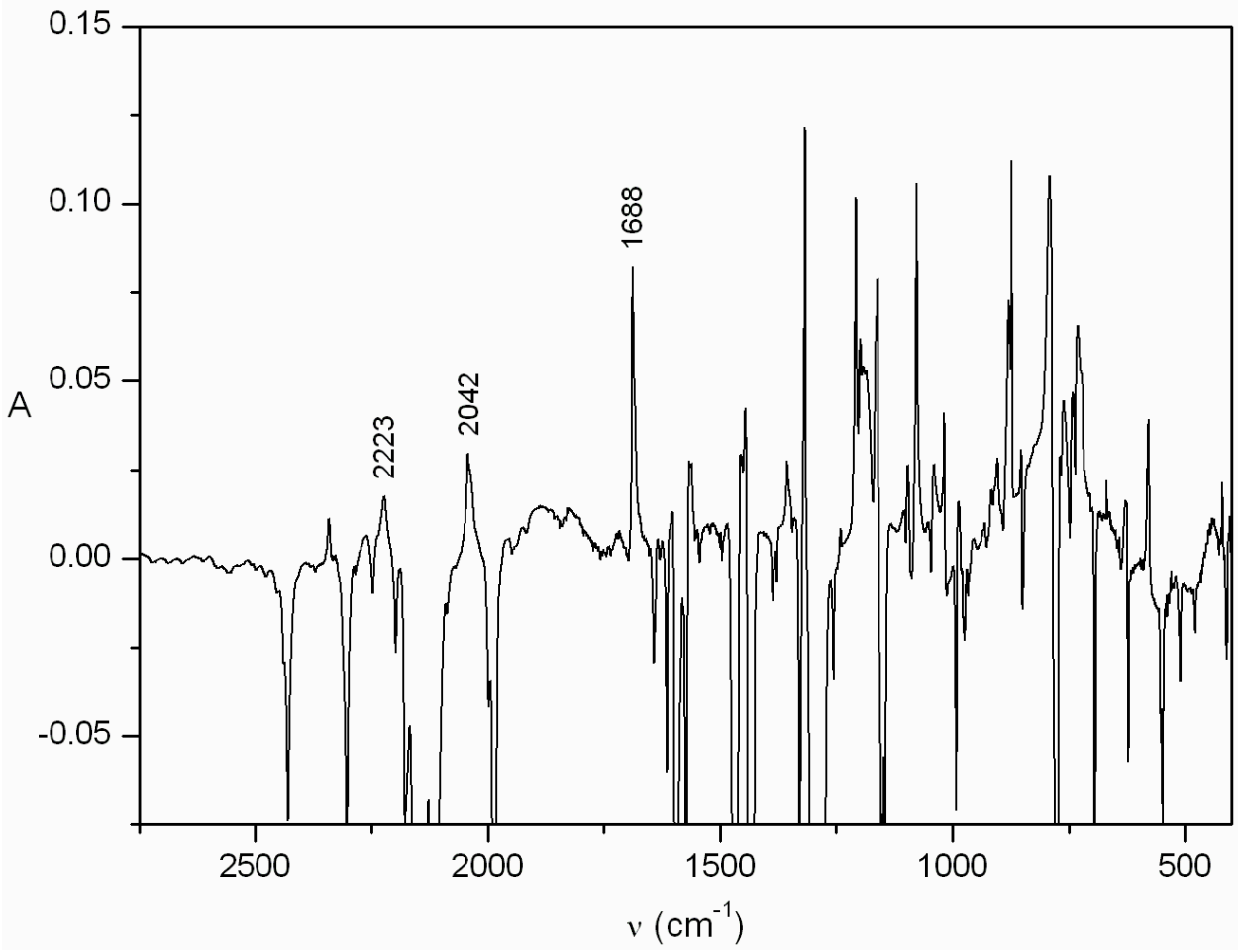



**Figure S13.** IR spectrum obtained after photolysis of 2-azidopyridine in Ar matrix at 254 nm (100 min), followed by 365 nm (310-390 nm interference filter) for 20 min. Negative bands are due to both 2-azidopyridine **22A** and diazacycloheptatetraene **21**. The same product bands are formed on photolysis of **21** at 308 nm (Figure 4). The product band at 2042 $cm^{-1}$ is possibly due to ketenimine **26** or **39**. Other, unmarked bands are at 1316, 1207, 1200, 1077, 872, 787, and 577 $cm^{-1}$.

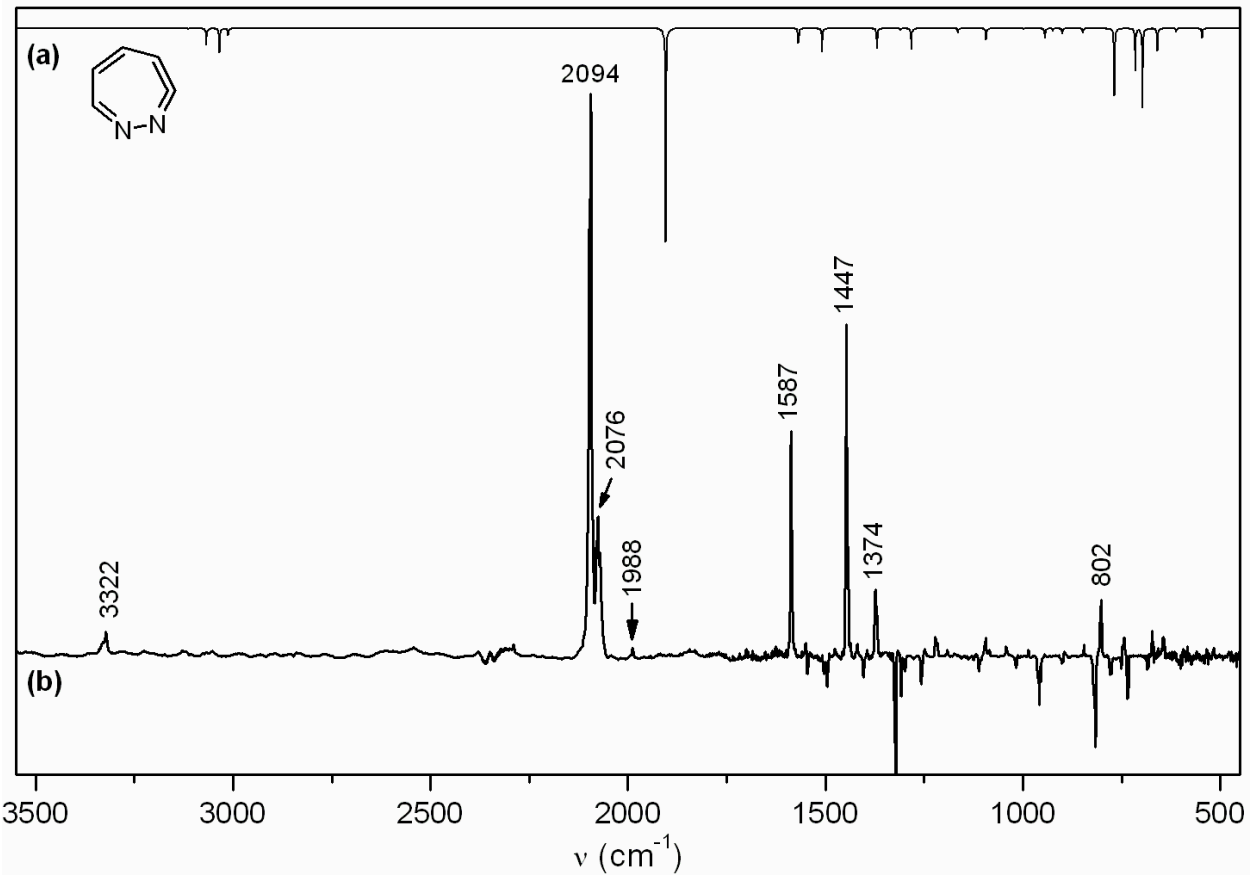



**Figure S14.** (a) Calculated spectrum of ketenimine **17** at the B3LYP/6-311G** level, wavenumbers scaled by 0.967. (b) Ar matrix IR spectrum resulting from photolysis of triazolopyridazine **8** at 222 nm for 2 min, showing prominent presence of diazo compounds and absence of **17**.

**Complete citation for reference 32:**

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara,

A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. *Gaussian 03, Revision E.01*; Gaussian, Inc., Wallingford CT, 2004.

**Complete citation for reference 36(b):**

Andersson, K.; Barysz, M.; Bernhardsson, A.; Blomberg, M. R. A.; Carissan, Y.; Cooper,D. L.; Cossi, M.; Devarajan, A.; Fülscher, M. P.; Gaenko, A.; Gagliardi, L.; de Graaf, C.; Hess, B. A.; Hagberg, D.; Karlström, G.; Krogh, J. W.; Lindh, R.; Malmqvist, P.-Å.; Nakajima, T.; Neogrády, P.; Olsen, J.; Pedersen, T. B.; Raab, J.; Roos, B. O.; Ryde, U.; Schimmelpfennig, B.; Schütz, M.; Seijo, L.; Serrano-Andrés, L.; Siegbahn, P. E. M.; Stålring, J.; Thorsteinsson, T.; Veryazov, V.; Widmark, P.-O. *MOLCAS*, version 7.2, University of Lund: Sweden, 2008.

**Computational Data**

## Table S1. Summary of the relative energies of species calculated at the B3LYP/6-31G*, CAS(8,8)/6-31G* and CASPT2//CAS(8,8)/6-31G* level

# Energies relative to triplet 2-pyridylnitrene **19T$_0$** in kcal/mol (or kJ/mol).

§ Relative energy of open-shell species where triplet contamination is non-negligible, i.e. $\langle S^2 \rangle \neq 0$ (UB3LYP/6-31G* only). For cases where $\langle S^2 \rangle \cong 1$, the energies were corrected using the Ziegler-Cramer's method (ref. 24); see notes to Table S2.

| Structure | Relative Energy (kcal/mol)# | | | Relative Energy (kJ/mol)# | | |
|---|---|---|---|---|---|---|
| | B3LYP | CASSCF | CASPT2 | B3LYP | CASSCF | CASPT2 |
| **10Z $T_0$** | 44.2 | -- | -- | 184.8 | -- | -- |
| **10Z $S_1$** | 55.0 | 58.9 | 64.4 | 230.2 | 246.4 | 269.4 |
| **10E $T_0$** | 45.6 | -- | -- | 191.0 | -- | -- |
| **10E $S_1$** | 59.0 | 62.4 | 68.1 | 246.7 | 261.1 | 284.9 |
| **10Z → 10E TS** | 61.8 | -- | -- | 258.5 | -- | -- |
| **10Z → 11Z TS** | 66.4 | -- | -- | 277.6 | -- | -- |
| **10Z → 16 TS** | 65.7 | 80.0 | 76.1 | 274.9 | 334.7 | 318.4 |
| **10E → 16 TS** | 69.0 | 82.9 | 76.6 | 288.9 | 346.9 | 320.5 |
| **10Z → 42 TS** | 68.6 | -- | -- | 287.0 | -- | -- |
| **10E → 42 TS** | 69.5 | -- | -- | 290.8 | -- | -- |
| **11Z** | 28.9 | -- | -- | 120.8 | -- | -- |
| **11E** | 26.5 | -- | -- | 111.0 | -- | -- |

| | | | | | | |
|---|---|---|---|---|---|---|
| **11Z → 11E TS** | 37.5 | -- | -- | 157.1 | -- | -- |
| **11Z → 12E TS** | 65.5 | -- | -- | 273.9 | -- | -- |
| **12Z $T_0$** + $N_2$ | 47.7 | -- | -- | 199.4 | -- | -- |
| **12Z $S_1$** + $N_2$ | 62.8 | -- | -- | 262.8 | -- | -- |
| **12E $T_0$** + $N_2$ | 47.7 | -- | -- | 199.5 | -- | -- |
| **12E $S_1$** + $N_2$ | 64.0 | -- | -- | 267.8 | -- | -- |
| **12E → 13 TS** + $N_2$ | 69.1 | -- | -- | 289.2 | -- | -- |
| **12E → 14 TS** + $N_2$ | 66.4 | -- | -- | 278.0 | -- | -- |
| **12E → 15 TS** + $N_2$ | 80.2 | -- | -- | 335.5 | -- | -- |
| **13** + $N_2$ | 4.4 | -- | -- | 18.2 | -- | -- |
| **14** + $N_2$ | 29.0 | -- | -- | 121.5 | -- | -- |
| **15** + $N_2$ | 15.1 | -- | -- | 63.2 | -- | -- |
| **16** | 51.2 | 66.6 | 50.7 | 214.3 | 278.6 | 212.2 |
| **16 → 17 TS** | 52.4 | 75.8 | 47.2 | 219.3 | 317.2 | 197.5 |
| **17** | 27.5 | 35.1 | 25.5 | 115.1 | 146.9 | 106.5 |
| **17 → 18 TS** | 40.9 | -- | -- | 171.3 | -- | -- |
| **17 → 19 $S_1$ TS** | -- | 62.3 | 40.0 | -- | 260.7 | 167.3 |
| **17 → 23 $S_1$ TS** | 39.6[§] | 39.4 | 39.0 | 165.9[§] | 164.8 | 163.0 |
| **17 → 17' TS** | 55.4 | -- | -- | 231.7 | -- | -- |
| **17'** | 47.1 | -- | -- | 196.9 | -- | -- |
| **18** | 34.3 | -- | -- | 143.4 | -- | -- |
| **18 → 19 TS** | 36.3 | -- | -- | 152.0 | -- | -- |
| **19 $T_0$** | 0 | 0 | 0 | 0 | 0 | 0 |
| **19 $S_1$** | 16.2[§] | 18.6 | 19.7 | 67.8[§] | 77.7 | 82.5 |
| **19 $S_2$** | 37.5 | 43.3 | 37.6 | 157.0 | 181.2 | 157.2 |
| **19 $S_1$ → 20 TS** | 22.5[§] | 44.0 | 45.1 | 94.1[§] | 184.1 | 188.7 |
| **19 $T_0$ → 23ZZ $T_0$ TS** | 29.0 | 31.8 | 36.5 | 121.3 | 133.1 | 152.7 |
| **19 $S_1$ → 23ZZ $S_1$ TS** | 24.2[§] | 26.4 | 22.7 | 101.1[§] | 110.5 | 95.0 |
| **19 → 32 TS** | 48.6 | -- | -- | 203.5 | -- | -- |
| **19 → 33 TS** | 52.3 | 67.7 | 47.3 | 218.8 | 283.3 | 197.8 |
| **20** | 13.1 | 18.1 | 10.1 | 55.0 | 75.6 | 42.2 |
| **20 → 21 TS** | 13.7 | 37.3 | 11.8 | 57.1 | 156.0 | 49.5 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **21** | 2.6 | 13.5 | 0.5 | 10.8 | 56.3 | 1.9 |
| **21 → 24 TS** | 49.0 | 70.4 | 46.7 | 205.0 | 294.6 | 195.4 |
| **23ZZ $T_0$** | 20.1 | 22.1 | 23.6 | 84.3 | 92.3 | 98.7 |
| **23ZZ $S_1$** | 16.3[§] | 29.4 | 30.8 | 68.2[§] | 122.9 | 128.9 |
| **23EZ $T_0$** | 15.7 | 16.3 | 18.1 | 65.8 | 68.1 | 75.8 |
| **23EZ $S_1$** | 11.9[§] | 23.6 | 25.3 | 49.7[§] | 98.6 | 106.1 |
| **23ZZ $T_0$ → 23EZ $T_0$ TS** | 24.8 | -- | -- | 104.0 | -- | -- |
| **23ZZ $S_1$ → 23EZ $S_1$ TS** | 24.6[§] | -- | -- | 102.9[§] | -- | -- |
| **23ZZ → 26Z TS** | 49.8 | 54.6 | 42.4 | 208.3 | 228.4 | 177.3 |
| **23ZZ → 27Z TS** | 49.0 | -- | -- | 205.1 | -- | -- |
| **23EZ → 27Z TS** | 45.5 | -- | -- | 190.3 | -- | -- |
| **23ZZ $S_1$ → 32 TS** | 29.1[§] | 29.5 | 30.4 | 121.8[§] | 123.3 | 127.1 |
| **24** | 20.8 | 25.0 | 12.7 | 87.0 | 104.7 | 53.3 |
| **24 → 25 TS** | 28.7 | 34.7 | 22.8 | 120.2 | 145.0 | 95.5 |
| **25** | 6.6 | 9.0 | 0.9 | 27.7 | 37.7 | 3.8 |
| **25 → 36 TS** | 43.7 | 51.5 | 42.0 | 183.0 | 215.5 | 175.8 |
| **25 → 38 $S_1$ TS** | 21.6[§] | -- | -- | 90.4[§] | -- | -- |
| **26Z** | -12.6 | -18.1 | -10.1 | -52.7 | -75.9 | -42.4 |
| **26Z → 27Z TS** | 30.7 | -- | -- | 128.4 | -- | -- |
| **27Z** | -28.7 | -- | -- | -120.3 | -- | -- |
| **27E** | -29.3 | -- | -- | -122.5 | -- | -- |
| **28** | -45.0 | -- | -- | -188.2 | -- | -- |
| **29** | -45.7 | -- | -- | -191.0 | -- | -- |
| **29 → 35 TS** | 1.5 | -- | -- | 6.3 | -- | -- |
| **30** | 9.9 | -7.5 | 5.5 | 41.6 | -31.5 | 22.9 |
| **32** | -22.9 | -42.9 | -32.4 | -96.0 | -179.4 | -135.5 |
| **32 → 28 TS** | 5.7 | -- | -- | 24.0 | -- | -- |
| **32 → 33 TS** | 17.9 | 30.0 | 10.3 | 74.8 | 125.4 | 43.0 |
| **32 → 34 TS** | 12.4 | -- | -- | 51.7 | -- | -- |
| **33** | -30.7 | -8.7 | -38.2 | -128.6 | -36.4 | -159.7 |
| **34** | -21.1 | -- | -- | -88.4 | -- | -- |
| **34 → 35 TS** | -0.0 | -- | -- | -0.1 | -- | -- |

| | | | | | | |
|---|---|---|---|---|---|---|
| **35** | -31.7 | -- | -- | -132.5 | -- | -- |
| **36** | 4.1 | 20.9 | 1.9 | 17.2 | 87.3 | 8.1 |
| **36 → 40 TS** | 45.6 | 62.4 | 42.1 | 190.7 | 260.9 | 176.2 |
| **36 → 41 TS** | 50.4 | -- | -- | 211.0 | -- | -- |
| **37Z $T_0$** | 27.4 | -- | -- | 114.6 | -- | -- |
| **37E $T_0$** | 27.4 | -- | -- | 114.8 | -- | -- |
| **38Z $T_0$** | 15.3 | 16.9 | 15.9 | 64.2 | 70.8 | 66.7 |
| **38Z $S_1$** | 19.4[§] | 25.5 | 24.1 | 81.2[§] | 106.5 | 100.8 |
| **38E $T_0$** | 12.5 | 14.4 | 12.9 | 52.4 | 60.2 | 54.1 |
| **38E $S_1$** | 16.3[§] | 21.8 | 20.2 | 68.2[§] | 91.1 | 84.6 |
| **38 $S_1$ → 32 TS** | 37.5 | 51.2 | 36.2 | 156.8 | 214.4 | 151.6 |
| **38Z $T_0$ → 38E $T_0$ TS** | 22.9 | -- | -- | 95.9 | -- | -- |
| **38Z $S_1$ → 38E $S_1$ TS** | 22.9[§] | -- | -- | 95.7[§] | -- | -- |
| **38 → 39 TS** | 43.4 | 59.5 | 42.2 | 181.8 | 249.1 | 176.7 |
| **39** | -14.8 | -1.2 | -13.6 | -62.0 | -5.2 | -56.8 |
| **39 → 28 TS** | 34.0 | -- | -- | 142.3 | -- | -- |
| **40** | -1.1 | -17.1 | -7.1 | -4.8 | -71.5 | -29.7 |
| **40 → 41 TS** | 28.6 | 40.2 | 27.4 | 119.7 | 168.4 | 114.8 |
| **41** | -21.6 | -- | -- | -90.5 | -- | -- |
| **41 → 28 TS** | 13.4 | -- | -- | 56.1 | -- | -- |
| **42** | 60.8 | -- | -- | 254.5 | -- | -- |
| **42 → 43 TS** | 60.6 | -- | -- | 253.5 | -- | -- |
| **43** | 39.9 | -- | -- | 166.8 | -- | -- |

## Table S2. Cartesian Coordinates and Calculated Energies (B3LYP/6-31G*)

Open-shell singlet species were computed at the UB3LYP/6-31G* level. In cases where $<S^2>=1$ (e.g. open-shell singlet nitrenes), the energy was corrected using the sum method of Cramer and Ziegler[1]: "The energy is computed as $E(S_1) = 2\,E(50{:}50) - E(T_0)$ where $E(50{:}50)$ is the energy of the broken symmetry unrestricted DFT wave function having an expectation value of 1 for the $<S^2>$ operator applied to a Slater determinant formed from the DFT orbitals (i.e., the exact wave function for the non-interacting Kohn–Sham reference system), and $E(T_0)$ is the energy of the triplet".

Natural spin densities[2] were computed at the UB3LYP/EPR-III level.

The UV-Vis spectra were calculated at the TD-B3LYP/6-311+G** level using Gaussian03, and convoluted using the SWizard program[3,4], revision 4.6, using the Lorentzian model. The half-bandwidths, $\Delta_{1/2,I}$, were taken to be equal to 3000 $cm^{-1}$.


(1). Johnson, W. T. G.; Sullivan, M. B.; Cramer, C. J. *Int. J. Quant. Chem.* **2001,** *85*, 492.

(2). NBO Version 3.1, Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. Gaussian 03, Revision E.01.

(3). S. I. Gorelsky, *SWizard program*, http://www.sg-chem.net/, University of Ottawa, Ottawa, Canada, 2009.

(4). S. I. Gorelsky, A. B. P. Lever, *J. Organomet. Chem.* **2001**, *635*, 187-196.

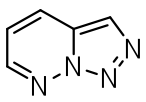

## Nitrogen ($N_2$)

| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 0.00000000 | 0.00000000 | 0.55275074 |
| N | 0.00000000 | 0.00000000 | -0.55275074 |

State=1-$\Sigma^+_g$
RB3LYP/6-31G(d), HF= -109.5241291
Zero-point correction= 0.005599 (Hartree/Particle)
Sum of electronic and zero-point Energies= -109.518530

## 8

[1,2,3]Triazolo[1,5-*b*]pyridazine

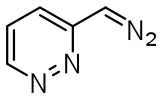


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | 0.28778315 | 0.76781820 | 0.00000000 |
| C | -0.96348815 | 1.42636700 | 0.00000000 |
| C | -2.09173133 | 0.64980057 | 0.00000000 |
| C | -1.95396545 | -0.77177028 | 0.00000000 |
| C | 1.64726027 | 1.05655870 | 0.00000000 |
| H | -1.00558980 | 2.51077729 | 0.00000000 |
| H | -3.08330072 | 1.08874273 | 0.00000000 |
| H | -2.83225797 | -1.41073809 | 0.00000000 |
| H | 2.14358511 | 2.01615028 | 0.00000000 |
| N | -0.81330840 | -1.41949565 | 0.00000000 |
| N | 0.27128778 | -0.62557724 | 0.00000000 |
| N | 1.51972036 | -1.13366599 | 0.00000000 |
| N | 2.33978987 | -0.10358523 | 0.00000000 |

State=1-A'
RB3LYP/6-31G(d), HF= -411.8661617
Zero-point correction= 0.093829 (Hartree/Particle)
Sum of electronic and zero-point Energies= -411.772332

## 9Z

(*s-Z*)-3-(diazomethyl)pyridazine




| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | 0.000000 | 0.412577 | 0.000000 |
| C | -1.236521 | 1.091201 | 0.000000 |
| C | -2.378089 | 0.317422 | 0.000000 |
| C | -2.216335 | -1.074288 | 0.000000 |
| H | -1.276313 | 2.177020 | 0.000000 |
| H | -3.368542 | 0.763199 | 0.000000 |
| H | -3.069684 | -1.746875 | 0.000000 |
| C | 1.247125 | 1.150179 | 0.000000 |
| N | 0.085131 | -0.935011 | 0.000000 |
| N | -1.021569 | -1.670242 | 0.000000 |
| N | 2.391830 | 0.520071 | 0.000000 |
| H | 1.302345 | 2.230632 | 0.000000 |
| N | 3.389623 | -0.030036 | 0.000000 |

State=1-A'
RB3LYP/6-31G(d), HF= -411.8443318
Zero-point correction= 0.090362 (Hartree/Particle)
Sum of electronic and zero-point Energies= -411.753970

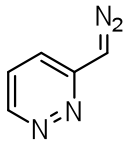
### Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A" | 84.8 | 1.9 | 0 |

| | | | | |
|---|---|---|---|---|
| 2 | A' | 121.7 | 0.0 | 0 |
| 3 | A" | 201.8 | 6.6 | 1 |
| 4 | A' | 319.0 | 4.9 | 1 |
| 5 | A" | 370.6 | 0.0 | 0 |
| 6 | A' | 446.3 | 1.1 | 0 |
| 7 | A" | 458.2 | 22.7 | 3 |
| 8 | A" | 517.3 | 2.7 | 0 |
| 9 | A" | 548.6 | 18.8 | 3 |
| 10 | A' | 624.4 | 0.0 | 0 |
| 11 | A' | 665.3 | 7.8 | 1 |
| 12 | A" | 737.8 | 7.4 | 1 |
| 13 | A" | 792.3 | 42.4 | 6 |
| 14 | A' | 836.4 | 8.1 | 1 |
| 15 | A" | 903.0 | 0.3 | 0 |
| 16 | A" | 970.2 | 0.1 | 0 |
| 17 | A' | 997.6 | 7.4 | 1 |
| 18 | A' | 1027.9 | 1.6 | 0 |
| 19 | A' | 1096.7 | 13.7 | 2 |
| 20 | A' | 1135.1 | 7.7 | 1 |
| 21 | A' | 1140.2 | 0.5 | 0 |
| 22 | A' | 1176.4 | 4.1 | 1 |
| 23 | A' | 1201.7 | 28.1 | 4 |
| 24 | A' | 1357.3 | 53.0 | 8 |
| 25 | A' | 1379.5 | 5.3 | 1 |
| 26 | A' | 1428.7 | 199.4 | 28 |
| 27 | A' | 1527.7 | 10.9 | 2 |
| 28 | A' | 1564.3 | 123.3 | 18 |
| 29 | A' | 2141.6 | 702.6 | 100 |
| 30 | A' | 3064.6 | 1.5 | 0 |
| 31 | A' | 3072.9 | 14.0 | 2 |
| 32 | A' | 3087.9 | 13.4 | 2 |
| 33 | A' | 3123.2 | 2.8 | 0 |

## 9E

(*s-E*)-3-(diazomethyl)pyridazine




| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | 0.000000 | 0.350046 | 0.000000 |
| C | 0.028845 | -1.060065 | 0.000000 |
| C | -1.185998 | -1.712981 | 0.000000 |
| C | -2.344429 | -0.925650 | 0.000000 |
| H | 0.969022 | -1.604462 | 0.000000 |
| H | -1.248839 | -2.797218 | 0.000000 |
| H | -3.335771 | -1.370416 | 0.000000 |
| C | 1.186609 | 1.185729 | 0.000000 |
| H | 1.105295 | 2.264805 | 0.000000 |
| N | -1.155659 | 1.050543 | 0.000000 |
| N | -2.319151 | 0.409182 | 0.000000 |

| | | | |
|---|---|---|---|
| N | 2.385334 | 0.679007 | 0.000000 |
| N | 3.432350 | 0.216243 | 0.000000 |

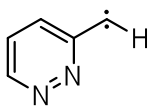
State=1-A'
RB3LYP/6-31G(d), HF= -411.8439885
Zero-point correction= 0.090395 (Hartree/Particle)
Sum of electronic and zero-point Energies= -411.753593

**Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):**

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A" | 79.3 | 2.2 | 0 |
| 2 | A' | 124.8 | 4.5 | 1 |
| 3 | A" | 203.1 | 9.0 | 1 |
| 4 | A' | 337.9 | 5.9 | 1 |
| 5 | A" | 371.1 | 0.0 | 0 |
| 6 | A" | 451.8 | 10.8 | 1 |
| 7 | A' | 453.7 | 0.1 | 0 |
| 8 | A" | 518.3 | 2.6 | 0 |
| 9 | A" | 588.4 | 33.2 | 5 |
| 10 | A' | 622.5 | 0.1 | 0 |
| 11 | A' | 665.0 | 7.9 | 1 |
| 12 | A" | 736.6 | 5.1 | 1 |
| 13 | A" | 791.3 | 40.8 | 6 |
| 14 | A' | 823.3 | 2.3 | 0 |
| 15 | A" | 903.7 | 0.0 | 0 |
| 16 | A" | 971.6 | 0.0 | 0 |
| 17 | A' | 993.8 | 7.5 | 1 |
| 18 | A' | 1025.6 | 2.6 | 0 |
| 19 | A' | 1086.3 | 20.5 | 3 |
| 20 | A' | 1128.3 | 17.3 | 2 |
| 21 | A' | 1146.7 | 3.7 | 1 |
| 22 | A' | 1162.0 | 1.7 | 0 |
| 23 | A' | 1228.9 | 18.5 | 3 |
| 24 | A' | 1338.8 | 10.5 | 1 |
| 25 | A' | 1394.1 | 23.5 | 3 |
| 26 | A' | 1421.2 | 183.2 | 25 |
| 27 | A' | 1525.3 | 1.1 | 0 |
| 28 | A' | 1564.3 | 74.9 | 10 |
| 29 | A' | 2114.2 | 733.8 | 100 |
| 30 | A' | 3066.2 | 0.6 | 0 |
| 31 | A' | 3074.0 | 10.2 | 1 |
| 32 | A' | 3089.2 | 11.0 | 1 |
| 33 | A' | 3122.0 | 13.6 | 2 |

## 10Z Triplet $T_0$

(*s-Z*)-3-pyridazinyl-carbene




| Atom | Coordinates (Angstroms) |
|---|---|

| Type | X | Y | Z |
|---|---|---|---|
| N | -1.217837 | -1.002591 | 0.000000 |
| N | -1.206535 | 0.319167 | 0.000000 |
| C | 0.000000 | 0.988460 | 0.000000 |
| C | 1.239748 | 0.290902 | 0.000000 |
| C | 1.197343 | -1.084789 | 0.000000 |
| C | -0.067124 | -1.691713 | 0.000000 |
| H | 2.173665 | 0.844276 | 0.000000 |
| H | 2.101833 | -1.685897 | 0.000000 |
| H | -0.179920 | -2.772349 | 0.000000 |
| C | -0.073490 | 2.383799 | 0.000000 |
| H | -0.903832 | 3.077983 | 0.000000 |

State=3-A"
<S2>= 2.036227
UB3LYP/6-31G(d), HF= -302.2673994
Zero-point correction= 0.077627 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.189773

## Natural Atomic Spin Densities (UB3LYP/EPR-III)

| | | |
|---|---|---|
| 1 | N | -0.07105 |
| 2 | N | 0.25975 |
| 3 | C | -0.14835 |
| 4 | C | 0.19103 |
| 5 | C | -0.08745 |
| 6 | C | 0.20491 |
| 7 | H | -0.00604 |
| 8 | H | 0.00296 |
| 9 | H | -0.00626 |
| 10 | C | 1.67529 |
| 11 | H | -0.01480 |

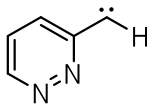
## Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A" | 179.2 | 5.1 | 16 |
| 2 | A' | 333.8 | 9.2 | 30 |
| 3 | A" | 348.5 | 0.0 | 0 |
| 4 | A" | 445.5 | 6.7 | 22 |
| 5 | A' | 555.6 | 1.0 | 3 |
| 6 | A" | 555.8 | 20.8 | 67 |
| 7 | A' | 615.6 | 1.3 | 4 |
| 8 | A" | 716.5 | 8.8 | 28 |
| 9 | A" | 778.4 | 30.7 | 99 |
| 10 | A' | 804.5 | 12.2 | 39 |
| 11 | A' | 852.4 | 8.4 | 27 |
| 12 | A" | 900.0 | 0.1 | 0 |
| 13 | A' | 937.4 | 4.9 | 16 |
| 14 | A" | 969.1 | 0.0 | 0 |
| 15 | A' | 1015.5 | 1.0 | 3 |
| 16 | A' | 1070.2 | 11.2 | 36 |
| 17 | A' | 1095.1 | 9.3 | 30 |
| 18 | A' | 1167.7 | 1.5 | 5 |
| 19 | A' | 1277.5 | 2.6 | 8 |

| | | | | |
|---|---|---|---|---|
| 20 | A' | 1297.7 | 4.5 | 15 |
| 21 | A' | 1387.8 | 6.1 | 20 |
| 22 | A' | 1493.8 | 10.0 | 32 |
| 23 | A' | 1530.0 | 9.0 | 29 |
| 24 | A' | 3069.0 | 1.1 | 3 |
| 25 | A' | 3080.3 | 10.2 | 33 |
| 26 | A' | 3092.2 | 8.3 | 27 |
| 27 | A' | 3136.6 | 4.6 | 15 |

## 10Z Singlet $S_1$

(*s-Z*)-3-pyridazinyl-carbene

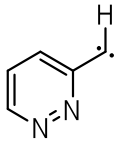


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -1.240931 | -0.989825 | 0.000000 |
| N | -1.201076 | 0.328311 | 0.000000 |
| C | 0.000000 | 0.986568 | 0.000000 |
| C | 1.222486 | 0.281773 | 0.000000 |
| C | 1.183059 | -1.103811 | 0.000000 |
| C | -0.083136 | -1.685346 | 0.000000 |
| H | 2.145841 | 0.851740 | 0.000000 |
| H | 2.080164 | -1.715572 | 0.000000 |
| H | -0.208804 | -2.765301 | 0.000000 |
| C | 0.029871 | 2.439719 | 0.000000 |
| H | -1.036835 | 2.746307 | 0.000000 |

State=1-A'
RB3LYP/6-31G(d), HF= -302.2499286
Zero-point correction= 0.077441 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.172487

## 10E Triplet $T_0$

(*s-E*)-3-pyridazinyl-carbene



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -1.291063 | -0.953506 | 0.000000 |
| N | -1.227345 | 0.364896 | 0.000000 |
| C | 0.000000 | 0.988942 | 0.000000 |
| C | 1.214280 | 0.240676 | 0.000000 |
| C | 1.117952 | -1.132774 | 0.000000 |
| C | -0.168512 | -1.689156 | 0.000000 |

| | | | |
|---|---|---|---|
| H | 2.172876 | 0.751196 | 0.000000 |
| H | 1.999224 | -1.767786 | 0.000000 |
| H | -0.324051 | -2.764423 | 0.000000 |
| C | 0.002466 | 2.386507 | 0.000000 |
| H | 0.783691 | 3.136109 | 0.000000 |

State=3-A"
<S2>= 2.036951
UB3LYP/6-31G(d), HF= -302.2649169
Zero-point correction= 0.077482 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.187434

**Natural Atomic Spin Densities (UB3LYP/EPR-III)**

| | | |
|---|---|---|
| 1 | N | -0.08604 |
| 2 | N | 0.24206 |
| 3 | C | -0.14936 |
| 4 | C | 0.21299 |
| 5 | C | -0.08583 |
| 6 | C | 0.20692 |
| 7 | H | -0.00653 |
| 8 | H | 0.00533 |
| 9 | H | -0.00686 |
| 10 | C | 1.68407 |
| 11 | H | -0.01676 |

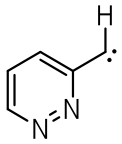
**Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):**

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A" | 175.5 | 4.8 | 15 |
| 2 | A' | 340.0 | 2.8 | 9 |
| 3 | A" | 348.5 | 1.2 | 4 |
| 4 | A" | 454.9 | 4.6 | 14 |
| 5 | A" | 506.7 | 13.6 | 43 |
| 6 | A' | 556.3 | 0.4 | 1 |
| 7 | A' | 616.6 | 0.0 | 0 |
| 8 | A" | 716.1 | 11.8 | 37 |
| 9 | A" | 773.5 | 32.4 | 101 |
| 10 | A' | 792.9 | 18.3 | 57 |
| 11 | A' | 844.1 | 6.8 | 21 |
| 12 | A" | 896.8 | 0.2 | 1 |
| 13 | A' | 962.9 | 1.6 | 5 |
| 14 | A" | 965.0 | 0.0 | 0 |
| 15 | A' | 1018.7 | 0.7 | 2 |
| 16 | A' | 1080.7 | 13.0 | 41 |
| 17 | A' | 1097.8 | 8.6 | 27 |
| 18 | A' | 1165.2 | 3.4 | 11 |
| 19 | A' | 1272.6 | 1.4 | 5 |
| 20 | A' | 1305.6 | 3.4 | 11 |
| 21 | A' | 1379.5 | 8.2 | 26 |
| 22 | A' | 1489.8 | 7.2 | 23 |
| 23 | A' | 1522.6 | 7.9 | 25 |
| 24 | A' | 3066.3 | 0.4 | 1 |
| 25 | A' | 3077.3 | 10.5 | 33 |
| 26 | A' | 3088.4 | 10.9 | 34 |

| | | | | |
|---|---|---|---|---|
| 27 | A' | 3131.4 | 0.5 | 1 |

## 10E Singlet $S_1$

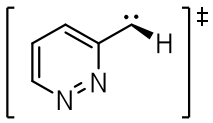
(*s-E*)-3-pyridazinyl-carbene



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -1.008878 | -1.244064 | 0.039633 |
| N | 0.307372 | -1.234297 | 0.014285 |
| C | 0.988575 | -0.043607 | 0.026696 |
| C | 0.299499 | 1.192486 | 0.044155 |
| C | -1.083569 | 1.176227 | -0.036383 |
| C | -1.687932 | -0.079081 | -0.026635 |
| H | 0.857078 | 2.122835 | 0.107563 |
| H | -1.677556 | 2.085124 | -0.064364 |
| H | -2.768727 | -0.188897 | -0.064871 |
| C | 2.425169 | -0.159298 | -0.107261 |
| H | 2.849294 | 0.809109 | 0.240818 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2433778
Zero-point correction= 0.077170 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.166208

## TS 10Z → 10E

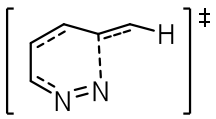


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -1.008401 | -1.230897 | 0.012305 |
| N | 0.316810 | -1.238189 | -0.010029 |
| C | 0.985090 | -0.042520 | -0.014131 |
| C | 0.301474 | 1.203420 | -0.008625 |
| C | -1.074915 | 1.161068 | 0.004402 |
| C | -1.698737 | -0.092606 | 0.011797 |
| H | 0.842522 | 2.144398 | -0.023491 |
| H | -1.661873 | 2.074679 | 0.012385 |
| H | -2.779265 | -0.199734 | 0.018532 |
| C | 2.411713 | -0.029790 | -0.139677 |
| H | 2.892011 | 0.066829 | 0.854041 |

State=1-A

RB3LYP/6-31G(d), HF= -302.2368432
Zero-point correction= 0.075123 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.161720
Imaginary frequency: -518.3 $cm^{-1}$

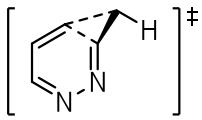
## TS 10Z → 11Z



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -0.92496483 | -1.22334613 | -0.00481600 |
| N | 0.30415818 | -1.31688096 | 0.00651800 |
| C | 1.11470698 | 0.15128816 | 0.01730500 |
| C | 0.21778782 | 1.25725903 | 0.02622400 |
| C | -1.14998315 | 1.10278584 | -0.01574300 |
| C | -1.74099398 | -0.16251824 | -0.00275200 |
| H | 0.64769968 | 2.24973609 | 0.10000100 |
| H | -1.78337128 | 1.98483775 | -0.02367500 |
| H | -2.80356695 | -0.35687839 | 0.04532200 |
| C | 2.41438899 | 0.04151634 | -0.13182000 |
| H | 3.14943306 | -0.43810056 | 0.50714600 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2288074
Zero-point correction= 0.074379 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.154428
Imaginary frequency: -666.7 $cm^{-1}$

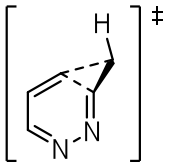
## TS 10Z → (16)17



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | 0.95195815 | -0.36949061 | -0.19872400 |
| C | 0.60229558 | 1.02757425 | -0.35190100 |
| C | -0.72156554 | 1.30560970 | 0.05111700 |
| C | -1.55754009 | 0.22973236 | 0.28638600 |
| H | 1.22211328 | 1.74985750 | -0.85974100 |
| H | -1.11377895 | 2.31947354 | 0.04694000 |
| H | -2.59109415 | 0.35210993 | 0.59276700 |
| N | -1.21322256 | -1.05719550 | -0.03303300 |
| N | 0.02351657 | -1.37863599 | -0.25075200 |
| C | 2.14058801 | -0.03098612 | 0.34985500 |
| H | 2.31628914 | -0.34526205 | 1.38612300 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2321226
Zero-point correction= 0.076643 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.155479
Imaginary frequency: -309.8 $cm^{-1}$

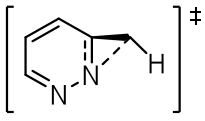
## TS 10E → (16)17



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | 0.97225145 | -0.38432816 | -0.21826200 |
| C | 0.57885649 | 1.02449935 | -0.41285814 |
| C | -0.72523129 | 1.26534711 | 0.03659788 |
| C | -1.48523813 | 0.15568006 | 0.40512621 |
| H | 1.15363304 | 1.71036107 | -1.02065388 |
| H | -1.18989619 | 2.24461142 | -0.05568812 |
| H | -2.48711345 | 0.23893734 | 0.81097388 |
| N | -1.14457523 | -1.09901801 | -0.01315068 |
| N | 0.05142514 | -1.40245698 | -0.39794802 |
| C | 1.89864869 | 0.03936898 | 0.61087293 |
| H | 2.73970389 | 0.71301099 | 0.61419775 |

State=1-A
RB3LYP/6-31G(d), HF= -302.226243
Zero-point correction= 0.076085 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.150158
Imaginary frequency: -381.8 $cm^{-1}$

## TS 10Z → 42

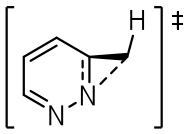


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 0.35052720 | -1.40884219 | 0.06547391 |
| N | -0.79890870 | -0.78131930 | -0.42908714 |
| C | -0.90726396 | 0.56334129 | -0.10757134 |
| C | 0.21746769 | 1.45991399 | -0.14119085 |
| C | 1.39699886 | 0.80275548 | -0.00191636 |
| C | 1.38975178 | -0.63507958 | 0.21848907 |
| H | 0.12382750 | 2.53754604 | -0.22814912 |

| | | | |
|---|---|---|---|
| H | 2.34712356 | 1.32967727 | 0.00146988 |
| H | 2.31673812 | -1.13464740 | 0.49306546 |
| C | -1.94705334 | 0.08476161 | 0.58237849 |
| H | -2.91358869 | -0.34032322 | 0.36962199 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2274457
Zero-point correction= 0.076580 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.150866
Imaginary frequency: -353.8 $cm^{-1}$

## TS 10E → 42

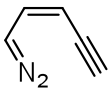



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 0.41736932 | -1.43058642 | 0.11735924 |
| N | -0.77153258 | -0.84874593 | -0.29351418 |
| C | -0.89634543 | 0.49912738 | -0.04032788 |
| C | 0.20452302 | 1.40689446 | -0.07031584 |
| C | 1.41892777 | 0.79180123 | -0.02284134 |
| C | 1.45941138 | -0.63844478 | 0.17155145 |
| H | 0.07302576 | 2.48380056 | -0.07702557 |
| H | 2.34754421 | 1.35444743 | -0.03870032 |
| H | 2.41132705 | -1.13084517 | 0.35816773 |
| C | -2.09797408 | 0.08749671 | 0.44561758 |
| H | -2.29357436 | 0.18412463 | 1.51826353 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2261215
Zero-point correction= 0.076718 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.149404
Imaginary frequency: -256.5 $cm^{-1}$

## 11Z

*(s-Z)-(Z)*-5-diazopent-3-en-1-yne




| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | 0.723687 | -1.445751 | 0.000000 |
| C | -0.692520 | -1.455190 | 0.000000 |
| C | -1.508915 | -0.368718 | 0.000000 |
| C | -1.206723 | 1.036979 | 0.000000 |

| | | | |
|---|---|---|---|
| H | -1.166925 | -2.434110 | 0.000000 |
| H | -2.579023 | -0.558993 | 0.000000 |
| H | -1.993341 | 1.781683 | 0.000000 |
| C | 1.935862 | -1.490206 | 0.000000 |
| H | 3.001801 | -1.503878 | 0.000000 |
| N | 1.032734 | 2.033302 | 0.000000 |
| N | 0.000000 | 1.545643 | 0.000000 |

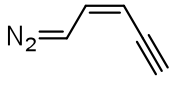
State=1-A'
RB3LYP/6-31G(d), HF= -302.2903369
Zero-point correction= 0.076177 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.214160

**Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):**

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A" | 51.6 | 1.7 | 1 |
| 2 | A' | 111.2 | 0.5 | 0 |
| 3 | A' | 180.4 | 0.3 | 0 |
| 4 | A" | 310.4 | 3.8 | 1 |
| 5 | A' | 359.0 | 8.1 | 3 |
| 6 | A" | 491.5 | 47.3 | 17 |
| 7 | A" | 503.9 | 6.7 | 2 |
| 8 | A' | 541.4 | 12.1 | 4 |
| 9 | A" | 562.8 | 45.3 | 16 |
| 10 | A" | 582.0 | 24.3 | 9 |
| 11 | A' | 661.8 | 35.7 | 13 |
| 12 | A" | 712.5 | 18.3 | 6 |
| 13 | A' | 771.1 | 9.0 | 3 |
| 14 | A' | 901.3 | 1.7 | 1 |
| 15 | A" | 930.3 | 0.0 | 0 |
| 16 | A' | 968.4 | 7.3 | 3 |
| 17 | A' | 1163.6 | 8.4 | 3 |
| 18 | A' | 1232.2 | 13.6 | 5 |
| 19 | A' | 1364.6 | 38.4 | 14 |
| 20 | A' | 1406.2 | 42.6 | 15 |
| 21 | A' | 1580.6 | 56.2 | 20 |
| 22 | A' | 2107.2 | 218.3 | 77 |
| 23 | A' | 2124.3 | 283.8 | 100 |
| 24 | A' | 3048.8 | 0.4 | 0 |
| 25 | A' | 3069.7 | 12.2 | 4 |
| 26 | A' | 3106.3 | 2.1 | 1 |
| 27 | A' | 3361.4 | 76.6 | 27 |

# 11E

*(s-E)-(Z)*-5-diazopent-3-en-1-yne




| Atom | Coordinates (Angstroms) | | |
|---|---|---|---|
| Type | X | Y | Z |
| C | 0.809372 | -2.008107 | 0.000000 |

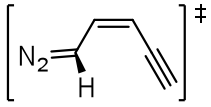
| | | | |
|---|---|---|---|
| C | -0.537013 | -1.566907 | 0.000000 |
| C | -0.912836 | -0.260986 | 0.000000 |
| H | -1.311555 | -2.329650 | 0.000000 |
| H | -1.974095 | -0.025328 | 0.000000 |
| C | 1.959027 | -2.395337 | 0.000000 |
| H | 2.967432 | -2.741115 | 0.000000 |
| C | 0.000000 | 0.846629 | 0.000000 |
| H | 1.076584 | 0.723599 | 0.000000 |
| N | -0.431619 | 2.079270 | 0.000000 |
| N | -0.806905 | 3.160836 | 0.000000 |

State=1-A'
RB3LYP/6-31G(d), HF= -302.2941193
Zero-point correction= 0.076212 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.217908

**Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):**

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A' | 98.7 | 0.5 | 0 |
| 2 | A" | 101.0 | 0.7 | 0 |
| 3 | A' | 201.9 | 4.0 | 1 |
| 4 | A" | 273.1 | 0.9 | 0 |
| 5 | A' | 350.1 | 10.9 | 2 |
| 6 | A" | 479.5 | 18.7 | 4 |
| 7 | A" | 502.4 | 6.6 | 1 |
| 8 | A' | 537.3 | 5.5 | 1 |
| 9 | A" | 577.0 | 66.1 | 13 |
| 10 | A" | 629.7 | 27.7 | 5 |
| 11 | A' | 662.9 | 35.6 | 7 |
| 12 | A' | 684.3 | 10.1 | 2 |
| 13 | A" | 711.1 | 23.9 | 5 |
| 14 | A' | 909.8 | 1.5 | 0 |
| 15 | A" | 928.5 | 1.1 | 0 |
| 16 | A' | 1082.6 | 13.3 | 3 |
| 17 | A' | 1160.5 | 8.9 | 2 |
| 18 | A' | 1213.6 | 20.4 | 4 |
| 19 | A' | 1300.4 | 11.8 | 2 |
| 20 | A' | 1410.6 | 43.5 | 8 |
| 21 | A' | 1573.7 | 159.8 | 30 |
| 22 | A' | 2109.2 | 509.7 | 97 |
| 23 | A' | 2121.0 | 526.2 | 100 |
| 24 | A' | 3055.6 | 1.2 | 0 |
| 25 | A' | 3071.8 | 8.1 | 2 |
| 26 | A' | 3104.3 | 5.6 | 1 |
| 27 | A' | 3361.6 | 93.6 | 18 |

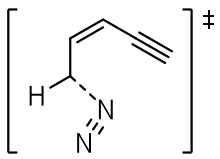
## TS 11Z → 11E



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | -1.833222 | -0.262523 | -0.078734 |
| C | -1.222746 | 0.991586 | -0.357708 |
| C | 0.037064 | 1.335961 | -0.030037 |
| H | -1.843727 | 1.722695 | -0.875756 |
| H | 0.375288 | 2.337120 | -0.301590 |
| C | -2.401862 | -1.310229 | 0.131901 |
| H | -2.881770 | -2.242221 | 0.327524 |
| C | 0.977806 | 0.456236 | 0.702725 |
| H | 1.057682 | 0.435446 | 1.784050 |
| N | 1.783825 | -0.332925 | 0.062039 |
| N | 2.494789 | -1.026964 | -0.511054 |

State=1-A
RB3LYP/6-31G(d), HF= -302.275703
Zero-point correction= 0.075345 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.200358
Imaginary frequency: -172.0 $cm^{-1}$

## TS 11Z → 12E

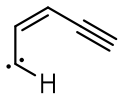



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | -1.48346122 | -0.07292679 | 0.10154913 |
| C | -1.01151363 | 1.22770815 | -0.15029894 |
| C | 0.25688358 | 1.67290583 | 0.14678890 |
| C | 1.24787335 | 0.88177515 | 0.79022002 |
| H | -1.69449957 | 1.89838665 | -0.67058393 |
| H | 0.46717220 | 2.71701902 | -0.11106486 |
| H | 2.26055252 | 1.23905514 | 0.54972048 |
| C | -1.92621813 | -1.18533166 | 0.30402540 |
| H | -2.30532486 | -2.15685140 | 0.52776512 |
| N | 1.11466550 | -1.84395788 | -0.63117801 |
| N | 1.56686536 | -0.84781262 | -0.43304254 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2271093
Zero-point correction= 0.071269 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.155840
Imaginary frequency: -194.4 $cm^{-1}$

## 12Z Triplet $T_0$

*(s-Z)-(Z)*-2-penten-4-yn-1-ylidene

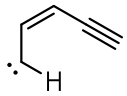


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | 1.71606748 | -0.94354380 | 0.00000000 |
| C | 1.38555825 | 0.36839475 | 0.00000000 |
| C | -1.09864544 | 0.14661636 | 0.00000000 |
| H | 2.19727779 | 1.09816448 | 0.00000000 |
| H | 1.17923623 | -1.88376217 | 0.00000000 |
| C | 0.07437757 | 0.90782646 | 0.00000000 |
| H | -0.02994384 | 1.99086109 | 0.00000000 |
| C | -2.12998489 | -0.50155062 | 0.00000000 |
| H | -3.03080802 | -1.07172231 | 0.00000000 |

State=3-A"
<S2>= 2.051086
UB3LYP/6-31G(d), HF= -192.7286523
Zero-point correction= 0.062963 (Hartree/Particle)
Sum of electronic and zero-point Energies= -192.665690

## 12Z Singlet $S_1$

*(s-Z)-(Z)*-2-penten-4-yn-1-ylidene

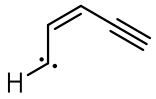


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | -1.77449366 | -0.72519171 | 0.19038333 |
| C | -1.35628298 | 0.54957701 | -0.17538208 |
| C | 1.07391006 | -0.02845037 | 0.00356144 |
| H | -2.06659442 | 1.37507003 | -0.23747208 |
| H | -1.06733043 | -1.52550270 | -0.08622365 |
| C | -0.01234769 | 0.86949939 | 0.02109127 |
| H | 0.23150520 | 1.88736923 | 0.33426049 |
| C | 2.06613450 | -0.72762370 | -0.02873390 |
| H | 2.92089827 | -1.36380027 | -0.07608507 |

State=1-A
RB3LYP/6-31G(d), HF= -192.704952
Zero-point correction= 0.063419 (Hartree/Particle)
Sum of electronic and zero-point Energies= -192.641533

## 12E Triplet $T_0$

*(s-E)-(Z)*-2-penten-4-yn-1-ylidene

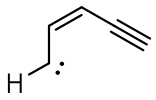


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | 1.62449916 | -1.03676163 | 0.00000000 |
| C | 1.35588879 | 0.29004137 | 0.00000000 |
| C | -1.13055560 | 0.18721957 | 0.00000000 |
| H | 2.20608348 | 0.98243721 | 0.00000000 |
| H | 2.52380166 | -1.63854990 | 0.00000000 |
| C | 0.07748763 | 0.89124932 | 0.00000000 |
| H | 0.02422273 | 1.97757942 | 0.00000000 |
| C | -2.19861659 | -0.39811674 | 0.00000000 |
| H | -3.12632814 | -0.92325811 | 0.00000000 |

State=3-A"
<S2>= 2.051399
UB3LYP/6-31G(d), HF= -192.7283154
Zero-point correction= 0.062672 (Hartree/Particle)
Sum of electronic and zero-point Energies= -192.665643

## 12E Singlet $S_1$

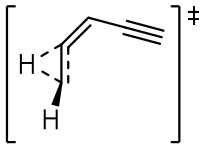
*(s-E)-(Z)*-2-penten-4-yn-1-ylidene



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | -1.66656514 | -0.86399617 | 0.06024863 |
| C | -1.32443553 | 0.50487549 | 0.07615811 |
| C | 1.10398721 | -0.01134693 | -0.02109552 |
| H | -2.04942264 | 1.32806943 | 0.07919649 |
| H | -2.66279794 | -0.98311280 | -0.41249681 |
| C | 0.00463471 | 0.87017615 | -0.01163839 |
| H | 0.24844797 | 1.92339812 | -0.16118478 |
| C | 2.12735177 | -0.66353263 | -0.01859483 |
| H | 2.99393455 | -1.28541026 | -0.01598286 |

State=1-A
RB3LYP/6-31G(d), HF= -192.7027392
Zero-point correction= 0.063097 (Hartree/Particle)
Sum of electronic and zero-point Energies= -192.639643

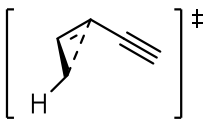
## TS 12E → 13



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | 0.17897991 | -0.80231967 | 0.00660310 |
| C | 1.19558636 | 0.08128442 | -0.04793177 |
| C | 1.87966897 | 1.23726268 | 0.12227706 |
| H | 0.40191636 | -1.86498894 | 0.00396685 |
| H | 2.30131703 | -0.28932889 | -0.04273162 |
| H | 2.29082996 | 1.65723750 | -0.81220262 |
| C | -1.17786185 | -0.39495266 | 0.02123143 |
| C | -2.34683759 | -0.07481367 | 0.03096353 |
| H | -3.37127820 | 0.21831374 | 0.05210727 |

State=1-A
RB3LYP/6-31G(d), HF= -192.6914978
Zero-point correction= 0.060010 (Hartree/Particle)
Sum of electronic and zero-point Energies= -192.631488
Imaginary frequency: -356.2 $cm^{-1}$

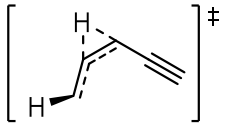
## TS 12E → 14



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | -0.11329345 | 0.77474740 | -0.11229385 |
| C | -1.42691798 | 0.40640090 | 0.24554767 |
| C | -1.47525521 | -0.88003725 | -0.17828435 |
| H | 0.01573734 | 1.75683870 | -0.58066148 |
| H | -2.20180961 | 1.14958126 | 0.45768211 |
| H | -2.35933356 | -1.18327783 | -0.75776189 |
| C | 1.07249075 | 0.02598870 | 0.01772496 |
| C | 2.18029593 | -0.45719049 | 0.13172799 |
| H | 3.12148552 | -0.94259766 | 0.25420670 |

State=1-A
RB3LYP/6-31G(d), HF= -192.6983526
Zero-point correction= 0.062589 (Hartree/Particle)
Sum of electronic and zero-point Energies= -192.635764
Imaginary frequency: -351.2 $cm^{-1}$

## TS 12E → 15

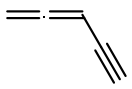


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | -2.22313077 | -0.59708822 | -0.31562174 |
| C | -1.20924118 | 0.12041092 | -0.01361679 |
| C | 1.27770545 | 0.12410711 | 0.05408453 |
| H | -1.16238844 | 0.59564487 | 1.04863541 |
| H | -3.01893645 | -1.02997959 | 0.27507279 |
| C | 0.05079273 | 0.78634292 | -0.07558476 |
| H | 0.04043896 | 1.87433181 | -0.06831940 |
| C | 2.35185552 | -0.43729014 | 0.15374360 |
| H | 3.28795437 | -0.94196535 | 0.22976548 |

State=1-A
RB3LYP/6-31G(d), HF= -192.672683
Zero-point correction= 0.058806 (Hartree/Particle)
Sum of electronic and zero-point Energies= -192.613877
Imaginary frequency: -835.1 $cm^{-1}$

## 13

Penta-1,2-dien-4-yne



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | -1.11562417 | 0.15114251 | 0.00000000 |
| C | 1.30864965 | 0.07870120 | 0.00000000 |
| C | 2.38947462 | -0.46537380 | 0.00000000 |
| H | 3.33434166 | -0.95908924 | 0.00000000 |
| C | -2.27801483 | -0.43821209 | 0.00000000 |
| H | -2.78563919 | -0.69850177 | -0.92763079 |
| H | -2.78563919 | -0.69850177 | 0.92763079 |
| C | 0.05490766 | 0.75816908 | 0.00000000 |
| H | 0.08057908 | 1.84953141 | 0.00000000 |

State=1-A'
RB3LYP/6-31G(d), HF= -192.800017
Zero-point correction= 0.065308 (Hartree/Particle)
Sum of electronic and zero-point Energies= -192.734709

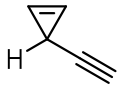
### Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A' | 136.0 | 1.5 | 2 |
| 2 | A" | 286.1 | 12.2 | 15 |
| 3 | A" | 338.1 | 0.0 | 0 |

| | | | | |
|---|---|---|---|---|
| 4 | A' | 347.3 | 2.2 | 3 |
| 5 | A' | 586.1 | 10.5 | 13 |
| 6 | A" | 605.5 | 29.1 | 36 |
| 7 | A" | 621.9 | 18.4 | 23 |
| 8 | A' | 667.7 | 41.8 | 52 |
| 9 | A' | 853.6 | 51.2 | 64 |
| 10 | A" | 855.4 | 19.9 | 25 |
| 11 | A' | 919.8 | 9.6 | 12 |
| 12 | A" | 971.2 | 0.0 | 0 |
| 13 | A' | 1102.0 | 0.8 | 1 |
| 14 | A' | 1307.8 | 6.6 | 8 |
| 15 | A' | 1416.4 | 4.0 | 5 |
| 16 | A' | 1974.3 | 57.8 | 72 |
| 17 | A' | 2137.0 | 3.5 | 4 |
| 18 | A' | 3008.5 | 1.2 | 1 |
| 19 | A' | 3012.1 | 4.5 | 6 |
| 20 | A" | 3078.5 | 1.1 | 1 |
| 21 | A' | 3363.7 | 79.8 | 100 |

## 14

3-Ethynylcycloprop-1-ene



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | 0.31305171 | 0.00000000 | 0.58568567 |
| H | 0.40655899 | 0.00000000 | 1.67557650 |
| C | -1.06318719 | 0.00000000 | 0.12692666 |
| C | 1.41538891 | 0.64590770 | -0.23358405 |
| C | -2.21561539 | 0.00000000 | -0.23969774 |
| H | -3.22819045 | 0.00000000 | -0.57309360 |
| C | 1.41538891 | -0.64590770 | -0.23358405 |
| H | 1.81573487 | -1.59090770 | -0.56848093 |
| H | 1.81573487 | 1.59090770 | -0.56848093 |

State=1-A'
RB3LYP/6-31G(d), HF=-192.7607009
Zero-point correction= 0.065337 (Hartree/Particle)
Sum of electronic and zero-point Energies= -192.695364

### Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A' | 198.3 | 3.2 | 4 |
| 2 | A" | 210.4 | 3.4 | 4 |
| 3 | A' | 511.8 | 14.3 | 18 |
| 4 | A" | 520.9 | 0.0 | 0 |
| 5 | A" | 614.7 | 47.2 | 59 |
| 6 | A' | 617.0 | 80.4 | 100 |
| 7 | A' | 661.9 | 44.1 | 55 |
| 8 | A" | 780.6 | 5.8 | 7 |

| | | | | |
|---|---|---|---|---|
| 9 | A" | 830.8 | 0.5 | 1 |
| 10 | A' | 876.8 | 9.8 | 12 |
| 11 | A' | 926.2 | 10.2 | 13 |
| 12 | A" | 971.4 | 43.0 | 54 |
| 13 | A" | 1011.9 | 3.0 | 4 |
| 14 | A' | 1117.5 | 1.6 | 2 |
| 15 | A' | 1323.5 | 8.9 | 11 |
| 16 | A' | 1676.0 | 32.7 | 41 |
| 17 | A' | 2135.7 | 5.6 | 7 |
| 18 | A' | 2973.3 | 34.4 | 43 |
| 19 | A" | 3143.2 | 1.0 | 1 |
| 20 | A' | 3190.8 | 0.3 | 0 |
| 21 | A' | 3362.3 | 66.2 | 83 |

## 15

Penta-1,4-diyne

**Error! Objects cannot be created from editing field codes.**

| Atom | Coordinates (Angstroms) | | |
|---|---|---|---|
| Type | X | Y | Z |
| C | -0.07238103 | 0.00000000 | 1.22966233 |
| C | -0.07238103 | 0.00000000 | -1.22966233 |
| C | 0.57491253 | 0.00000000 | -2.24715462 |
| H | 1.15646847 | 0.00000000 | -3.14091375 |
| C | 0.57491253 | 0.00000000 | 2.24715462 |
| H | 1.15646847 | 0.00000000 | 3.14091375 |
| C | -0.87670122 | 0.00000000 | 0.00000000 |
| H | -1.54131986 | -0.87640746 | 0.00000000 |
| H | -1.54131986 | 0.87640746 | 0.00000000 |

State=1-A1
RB3LYP/6-31G(d), HF= -192.7828784
Zero-point correction= 0.065320 (Hartree/Particle)
Sum of electronic and zero-point Energies= -192.717559

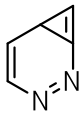
### Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A1 | 132.1 | 1.0 | 1 |
| 2 | B1 | 296.6 | 16.5 | 17 |
| 3 | A2 | 316.4 | 0.0 | 0 |
| 4 | B2 | 322.8 | 3.9 | 4 |
| 5 | A1 | 543.2 | 8.9 | 9 |
| 6 | A2 | 647.8 | 0.0 | 0 |
| 7 | B1 | 650.1 | 89.8 | 91 |
| 8 | B2 | 666.3 | 26.5 | 27 |
| 9 | A1 | 668.0 | 53.7 | 54 |
| 10 | A1 | 872.9 | 8.4 | 9 |
| 11 | B1 | 900.6 | 0.6 | 1 |
| 12 | B2 | 965.7 | 4.7 | 5 |
| 13 | A2 | 1202.4 | 0.0 | 0 |
| 14 | B2 | 1296.5 | 19.5 | 20 |

| | | | | |
|---|---|---|---|---|
| 15 | A1 | 1407.3 | 6.6 | 7 |
| 16 | B2 | 2158.0 | 2.6 | 3 |
| 17 | A1 | 2163.4 | 0.1 | 0 |
| 18 | A1 | 2913.1 | 8.1 | 8 |
| 19 | B1 | 2935.9 | 2.5 | 3 |
| 20 | B2 | 3362.4 | 98.8 | 100 |
| 21 | A1 | 3363.4 | 30.5 | 31 |

## (16)

2,3-Diazabicyclo[4.1.0]hepta-1(7),2,4-triene



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 0.0004568955 | 0.0003464216 | -0.0019091652 |
| N | 0.0007806039 | -0.0024063969 | 1.2969470911 |
| C | 1.2596367178 | -0.0000188180 | 1.7937953826 |
| C | 2.4947844638 | -0.8290028756 | 1.1870178278 |
| C | 2.3048404114 | -0.7844608764 | -0.2361269561 |
| C | 1.1531250797 | -0.1990471234 | -0.7343960178 |
| C | 2.4488041910 | 0.4602095955 | 1.9911100346 |
| H | 3.0254035177 | 1.3671291402 | 2.1004668336 |
| H | 2.8640500336 | -1.7417837577 | 1.6580747473 |
| H | 2.9439753504 | -1.3480856852 | -0.9154769450 |
| H | 0.9913139910 | -0.1023952671 | -1.8033867118 |

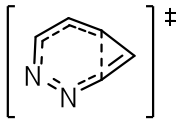
State=1-A
RB3LYP/6-31G(d), HF= -302.2566037
RMSD=4.843e-09|RMSF=1.790e-04, unstable wavefunction.
Zero-point correction= 0.078048 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.178555

### Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A | 155.9 | 15.8 | 39 |
| 2 | A | 273.5 | 4.2 | 10 |
| 3 | A | 338.9 | 7.5 | 18 |
| 4 | A | 440.2 | 11.5 | 28 |
| 5 | A | 569.5 | 30.7 | 75 |
| 6 | A | 580.3 | 14.5 | 35 |
| 7 | A | 639.7 | 9.6 | 23 |
| 8 | A | 700.6 | 16.0 | 39 |
| 9 | A | 786.4 | 32.1 | 78 |
| 10 | A | 856.5 | 4.7 | 11 |
| 11 | A | 895.0 | 16.1 | 39 |
| 12 | A | 924.5 | 3.8 | 9 |
| 13 | A | 945.9 | 17.2 | 42 |
| 14 | A | 953.2 | 3.2 | 8 |
| 15 | A | 995.7 | 1.8 | 4 |

| | | | | |
|---|---|---|---|---|
| 16 | A | 998.7 | 19.8 | 48 |
| 17 | A | 1087.9 | 9.6 | 23 |
| 18 | A | 1165.4 | 7.0 | 17 |
| 19 | A | 1267.8 | 32.1 | 78 |
| 20 | A | 1312.6 | 26.2 | 64 |
| 21 | A | 1403.1 | 2.7 | 7 |
| 22 | A | 1475.5 | 4.0 | 10 |
| 23 | A | 1793.1 | 41.2 | 101 |
| 24 | A | 3007.5 | 27.0 | 66 |
| 25 | A | 3038.8 | 12.3 | 30 |
| 26 | A | 3089.5 | 10.7 | 26 |
| 27 | A | 3160.9 | 4.5 | 11 |

## TS (16) → 17



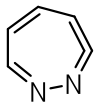
| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 1.5708803825 | -0.2620421970 | 0.0469559786 |
| C | -0.4573390459 | -1.0816968260 | -0.1425435083 |
| C | -1.4652832614 | -0.6534026869 | 0.5498231926 |
| C | -1.2808943269 | 0.4861262129 | -0.3724917463 |
| C | -0.2338765274 | 1.4013652737 | -0.0808233804 |
| C | 1.0346733565 | 0.9621676935 | 0.2873620270 |
| H | -1.9392018530 | -0.8135607202 | 1.4949959710 |
| H | -1.9697338860 | 0.6745104822 | -1.1790107009 |
| H | -0.3506969404 | 2.4482396373 | -0.3053533925 |
| H | 1.7778323363 | 1.6849792582 | 0.5660259319 |
| N | 0.8431366423 | -1.2638901831 | -0.3361870239 |

State=1-A
CAS(8,8)/6-31G(d), HF= -300.4724878
Zero-point correction= 0.082085 (Hartree/Particle)
Sum of electronic and zero-point Energies= -300.390402
Imaginary frequency: -758.0 $cm^{-1}$

Single Point Energy on CAS(8,8)/6-31G* Geometry (above):
RB3LYP/6-31G(d), HF= -302.254594, RMSD=6.200e-09|RMSF=8.729e-03
Zero-point correction= 0.077934 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.176660
Imaginary frequency: -462.0 $cm^{-1}$

## 17

1,2-Diazacyclohepta-2,3,5,7-tetraene



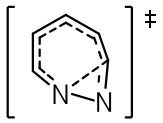
| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | 0.91083661 | -0.92374448 | -0.07864955 |
| C | 0.85142385 | 1.35094135 | -0.09432091 |
| C | -0.50923456 | 1.32352269 | -0.17419152 |
| C | -1.37358076 | 0.21671002 | 0.26608828 |
| H | 1.38587930 | 2.28022677 | -0.29190980 |
| H | -1.03696774 | 2.23823833 | -0.43315839 |
| H | -2.30787995 | 0.52852128 | 0.73829289 |
| N | -1.25235766 | -1.07197641 | 0.23257852 |
| N | -0.08066981 | -1.49024527 | -0.55731049 |
| C | 1.58800076 | 0.15409506 | 0.30583043 |
| H | 2.48548537 | 0.15941753 | 0.91135882 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2956515
Zero-point correction= 0.079326 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.216326

**Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):**

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A | 298.7 | 0.0 | 0 |
| 2 | A | 311.7 | 0.1 | 0 |
| 3 | A | 352.9 | 11.2 | 8 |
| 4 | A | 442.1 | 0.7 | 1 |
| 5 | A | 546.6 | 5.7 | 4 |
| 6 | A | 612.9 | 1.8 | 1 |
| 7 | A | 659.3 | 14.0 | 10 |
| 8 | A | 697.5 | 49.6 | 37 |
| 9 | A | 715.8 | 25.9 | 19 |
| 10 | A | 768.1 | 41.8 | 31 |
| 11 | A | 848.8 | 2.3 | 2 |
| 12 | A | 900.7 | 2.9 | 2 |
| 13 | A | 924.9 | 1.0 | 1 |
| 14 | A | 944.7 | 5.9 | 4 |
| 15 | A | 999.6 | 0.2 | 0 |
| 16 | A | 1093.1 | 6.7 | 5 |
| 17 | A | 1164.3 | 2.2 | 2 |
| 18 | A | 1282.4 | 12.8 | 9 |
| 19 | A | 1310.2 | 1.0 | 1 |
| 20 | A | 1369.3 | 12.1 | 9 |
| 21 | A | 1508.9 | 14.4 | 11 |
| 22 | A | 1568.4 | 9.2 | 7 |
| 23 | A | 1904.6 | 134.6 | 100 |
| 24 | A | 3012.2 | 4.2 | 3 |
| 25 | A | 3034.2 | 14.8 | 11 |
| 26 | A | 3067.2 | 10.3 | 8 |
| 27 | A | 3114.1 | 0.1 | 0 |

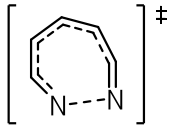
## TS 17 → 18



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 1.34026513 | 0.32232275 | -0.47929559 |
| N | 1.43154487 | -0.83392917 | 0.61691284 |
| C | 0.42441234 | -1.08313834 | -0.04727307 |
| C | 0.47489779 | 1.30918432 | -0.12725822 |
| C | -0.84636104 | 1.18784160 | 0.29595055 |
| C | -1.57000574 | -0.01000405 | 0.07466012 |
| C | -0.94326247 | -1.19733814 | -0.27024393 |
| H | 0.83618328 | 2.28977604 | -0.44227878 |
| H | -1.39575383 | 2.09483444 | 0.52529106 |
| H | -2.65683430 | 0.02984995 | 0.08420326 |
| H | -1.42435040 | -2.07248794 | -0.68554902 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2725673
Zero-point correction= 0.077627 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.194940
Imaginary frequency: -516.9 $cm^{-1}$

## TS 17 → 23ZZ $S_1$

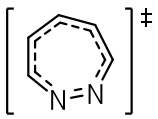


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 1.18720850 | -1.35351246 | -0.46558335 |
| N | 1.72734231 | 0.47872137 | 0.31392944 |
| C | 0.76813008 | 1.28996970 | 0.13278961 |
| C | -0.64441552 | 1.28483751 | -0.26190006 |
| C | -1.55834161 | 0.27950369 | -0.02250512 |
| C | -1.19869013 | -1.04517100 | 0.33307561 |
| C | 0.08674584 | -1.38555092 | -0.00710895 |
| H | 1.07597035 | 2.29752972 | 0.46872095 |
| H | -1.03014448 | 2.27004249 | -0.50486005 |
| H | -2.61753591 | 0.53147252 | -0.06211045 |
| H | -1.87137166 | -1.72865388 | 0.83638451 |

State=1-A
<S2>= 0.483871, i.e. 75.8% singlet
UB3LYP/6-31G(d), HF= -302.2726391
Zero-point correction= 0.075638 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.197001

Imaginary frequency: -437.6 $cm^{-1}$

## TS 17 → 17’

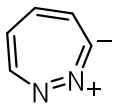


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | -1.28226039 | 0.78697028 | 0.12961061 |
| C | -0.05148055 | 1.42759437 | 0.02041617 |
| C | 1.26905527 | 0.86540296 | -0.11038302 |
| C | 1.65790775 | -0.44251991 | 0.06826182 |
| C | 0.56618908 | -1.35755305 | 0.25417901 |
| N | -0.56307578 | -1.28902985 | -0.21128739 |
| N | -1.64930049 | -0.49134829 | -0.16652571 |
| H | -2.14433180 | 1.41282152 | 0.35869581 |
| H | -0.08653900 | 2.51016005 | 0.09690770 |
| H | 2.07253589 | 1.59857024 | -0.19637485 |
| H | 2.68850183 | -0.73827275 | 0.21295552 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2489988
Zero-point correction= 0.077070 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.171929
Imaginary frequency: -630.8 $cm^{-1}$

## 17’

1,2-Diazacyclohepta-1,2,4,6-tetraen-2-ylium-3-ide



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | -1.45739640 | 0.53920432 | 0.10386571 |
| C | -0.38430799 | 1.36181112 | 0.17634929 |
| C | 1.01190880 | 1.05753371 | -0.19390037 |
| C | 1.64195427 | -0.13790554 | -0.09069505 |
| C | 0.85365596 | -1.25153155 | 0.51872320 |
| N | -0.25515689 | -1.25552566 | -0.02710137 |
| N | -1.35331096 | -0.78964004 | -0.41491153 |
| H | -2.46298265 | 0.86488930 | 0.35366405 |
| H | -0.57444496 | 2.38838249 | 0.48214112 |
| H | 1.61339210 | 1.91910167 | -0.47987368 |
| H | 2.68842259 | -0.27088591 | -0.34789783 |

State=1-A

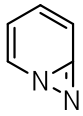
RB3LYP/6-31G(d), HF= -302.2644795
Zero-point correction= 0.079304 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.185176

**Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):**

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A | 278.6 | 15.5 | 5 |
| 2 | A | 320.0 | 7.5 | 2 |
| 3 | A | 366.5 | 23.8 | 7 |
| 4 | A | 416.2 | 3.3 | 1 |
| 5 | A | 524.0 | 13.9 | 4 |
| 6 | A | 584.9 | 6.7 | 2 |
| 7 | A | 657.3 | 20.6 | 6 |
| 8 | A | 724.9 | 37.9 | 12 |
| 9 | A | 797.4 | 14.8 | 5 |
| 10 | A | 841.9 | 3.5 | 1 |
| 11 | A | 870.8 | 2.5 | 1 |
| 12 | A | 931.2 | 14.7 | 5 |
| 13 | A | 940.3 | 12.6 | 4 |
| 14 | A | 951.8 | 15.9 | 5 |
| 15 | A | 961.4 | 4.0 | 1 |
| 16 | A | 1142.2 | 9.0 | 3 |
| 17 | A | 1157.6 | 6.8 | 2 |
| 18 | A | 1206.7 | 7.6 | 2 |
| 19 | A | 1302.5 | 28.3 | 9 |
| 20 | A | 1361.3 | 0.7 | 0 |
| 21 | A | 1530.4 | 3.1 | 1 |
| 22 | A | 1569.9 | 1.7 | 1 |
| 23 | A | 1771.8 | 322.2 | 100 |
| 24 | A | 3042.7 | 3.5 | 1 |
| 25 | A | 3057.9 | 3.2 | 1 |
| 26 | A | 3088.1 | 17.3 | 5 |
| 27 | A | 3092.3 | 6.3 | 2 |

# 18

1,7-diazabicyclo[4.1.0]hepta-2,4,6-triene



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -0.88984891 | -0.77451711 | -0.51733400 |
| C | -0.89302507 | 0.57317989 | -0.11727700 |
| C | 0.25843683 | 1.44333603 | -0.15071700 |
| C | 1.41330491 | 0.74823417 | 0.02960700 |
| C | 1.39604708 | -0.69191883 | 0.21568000 |
| C | 0.25343917 | -1.40276497 | -0.00917900 |
| H | 0.19292670 | 2.51992102 | -0.25026000 |
| H | 2.36501185 | 1.27126628 | 0.07083600 |
| H | 2.32286515 | -1.20690272 | 0.44775000 |

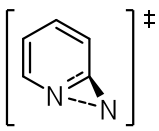
| | | | |
|---|---|---|---|
| H | 0.23512830 | -2.48946597 | -0.00316800 |
| N | -1.92231502 | 0.18662777 | 0.50678500 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2847793
Zero-point correction= 0.079234 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.205545

**Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):**

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A | 162.7 | 3.4 | 9 |
| 2 | A | 291.9 | 4.3 | 11 |
| 3 | A | 400.2 | 2.2 | 6 |
| 4 | A | 461.5 | 7.5 | 20 |
| 5 | A | 548.3 | 5.7 | 15 |
| 6 | A | 587.4 | 2.6 | 7 |
| 7 | A | 657.0 | 4.8 | 13 |
| 8 | A | 709.3 | 37.6 | 99 |
| 9 | A | 790.3 | 16.8 | 44 |
| 10 | A | 850.4 | 4.8 | 13 |
| 11 | A | 862.3 | 16.5 | 43 |
| 12 | A | 924.7 | 3.4 | 9 |
| 13 | A | 950.6 | 1.7 | 4 |
| 14 | A | 955.5 | 1.5 | 4 |
| 15 | A | 1034.8 | 5.1 | 13 |
| 16 | A | 1100.4 | 22.3 | 59 |
| 17 | A | 1131.5 | 5.4 | 14 |
| 18 | A | 1177.7 | 16.2 | 43 |
| 19 | A | 1322.0 | 7.0 | 18 |
| 20 | A | 1384.3 | 3.7 | 10 |
| 21 | A | 1464.8 | 23.2 | 61 |
| 22 | A | 1568.9 | 5.8 | 15 |
| 23 | A | 1725.6 | 37.7 | 99 |
| 24 | A | 3069.8 | 1.2 | 3 |
| 25 | A | 3076.3 | 9.9 | 26 |
| 26 | A | 3094.0 | 11.1 | 29 |
| 27 | A | 3114.9 | 0.4 | 1 |

## TS 18 → 19



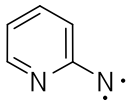

| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | 1.64978844 | 0.24297472 | 0.02246635 |
| C | 0.80704589 | 1.39768419 | 0.03692458 |
| H | 2.72960864 | 0.35515589 | 0.01440412 |
| H | 1.25346488 | 2.38830782 | 0.02955024 |
| N | -2.07258091 | -0.71800307 | -0.47152203 |

| | | | |
|---|---|---|---|
| C | 1.08360029 | -1.01827929 | 0.09827517 |
| H | 1.70381981 | -1.91189793 | 0.13076057 |
| N | -0.23513795 | -1.19734512 | 0.34371944 |
| C | -1.04188967 | -0.11763097 | 0.00776039 |
| C | -0.54802693 | 1.24481594 | -0.02582408 |
| H | -1.23596941 | 2.07848401 | -0.11771130 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2809623
Zero-point correction= 0.078693 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.202269
Imaginary frequency: -180.0 $cm^{-1}$

## 19 Triplet $T_0$

2-Pyridyl-nitrene



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 0.03417588 | 2.36339355 | 0.00000000 |
| N | -1.22817577 | 0.41257822 | 0.00000000 |
| C | 0.00000551 | 1.02679621 | 0.00000000 |
| C | 1.22643033 | 0.29240292 | 0.00000000 |
| C | 1.17100820 | -1.09252788 | 0.00000000 |
| C | -0.07960282 | -1.71668268 | 0.00000000 |
| C | -1.23528062 | -0.91111852 | 0.00000000 |
| H | 2.16716573 | 0.83272946 | 0.00000000 |
| H | 2.08489222 | -1.68005814 | 0.00000000 |
| H | -0.17051082 | -2.79825473 | 0.00000000 |
| H | -2.21883984 | -1.37969839 | 0.00000000 |

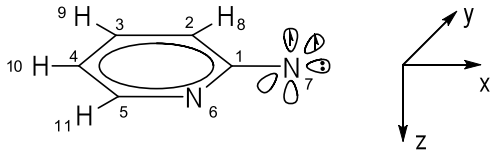
State=3-A"
<S2>= 2.047859
UB3LYP/6-31G(d), HF=-302.3397371
Zero-point correction= 0.079560 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.260177

### Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A" | 185.2 | 0.4 | 1 |
| 2 | A' | 372.2 | 2.9 | 6 |
| 3 | A" | 385.3 | 3.7 | 7 |
| 4 | A" | 473.2 | 0.3 | 1 |
| 5 | A' | 532.6 | 1.2 | 2 |
| 6 | A' | 604.9 | 4.4 | 9 |
| 7 | A" | 697.4 | 14.8 | 30 |
| 8 | A" | 759.5 | 50.4 | 101 |
| 9 | A' | 828.1 | 1.5 | 3 |
| 10 | A" | 852.6 | 0.9 | 2 |

| | | | | |
|---|---|---|---|---|
| 11 | A' | 930.6 | 10.3 | 21 |
| 12 | A" | 952.0 | 0.7 | 1 |
| 13 | A" | 968.3 | 0.3 | 1 |
| 14 | A' | 1009.8 | 4.1 | 8 |
| 15 | A' | 1068.4 | 5.8 | 12 |
| 16 | A' | 1123.1 | 0.3 | 1 |
| 17 | A' | 1190.4 | 11.1 | 22 |
| 18 | A' | 1211.2 | 4.0 | 8 |
| 19 | A' | 1306.9 | 7.0 | 14 |
| 20 | A' | 1370.6 | 11.7 | 23 |
| 21 | A' | 1397.9 | 0.4 | 1 |
| 22 | A' | 1504.2 | 25.6 | 51 |
| 23 | A' | 1526.3 | 0.4 | 1 |
| 24 | A' | 3039.3 | 18.2 | 36 |
| 25 | A' | 3071.9 | 4.9 | 10 |
| 26 | A' | 3092.0 | 8.7 | 17 |
| 27 | A' | 3098.2 | 3.7 | 7 |

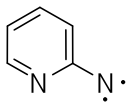
**Natural Atomic Spin Densities (UB3LYP/EPR-III)**




| Net Natural Atomic Valence Orbitals Population | | | | | | |
|---|---|---|---|---|---|---|
| | | 2s | 2p | | | Total |
| | | | px | py | pz | |
| C | 1 | -0.01785 | -0.02703 | -0.01666 | -0.13411 | -0.19565 |
| C | 2 | 0.02466 | 0.01175 | 0.01813 | 0.23877 | 0.29331 |
| C | 3 | -0.00562 | -0.00345 | -0.00528 | -0.09190 | -0.10625 |
| C | 4 | 0.01174 | 0.00575 | 0.00600 | 0.24699 | 0.27048 |
| C | 5 | -0.00555 | -0.00253 | -0.00476 | -0.07671 | -0.08955 |
| N | 6 | 0.01878 | 0.01111 | 0.01532 | 0.17765 | 0.22286 |
| N | 7 | 0.02799 | 0.01121 | 0.92904 | 0.63359 | 1.60183 |
| H | 8 | -0.00901 | (1s) | | | -0.00901 |
| H | 9 | 0.00535 | (1s) | | | 0.00535 |
| H | 10 | -0.00832 | (1s) | | | -0.00832 |
| H | 11 | 0.00453 | (1s) | | | 0.00453 |

## 19 Open-Shell Singlet $S_1$

2-Pyridyl-nitrene



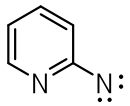

Atom Coordinates (Angstroms)

| Type | X | Y | Z |
|---|---|---|---|
| N | 0.04000623 | 2.35006018 | 0.00000000 |
| N | -1.24020101 | 0.41110749 | 0.00000000 |
| C | -0.00271628 | 1.03817793 | 0.00000000 |
| C | 1.23182707 | 0.29047304 | 0.00000000 |
| C | 1.17521221 | -1.09026941 | 0.00000000 |
| C | -0.07766303 | -1.71544307 | 0.00000000 |
| C | -1.23829955 | -0.90681009 | 0.00000000 |
| H | 2.17141507 | 0.83208064 | 0.00000000 |
| H | 2.08851239 | -1.67877596 | 0.00000000 |
| H | -0.16929244 | -2.79678528 | 0.00000000 |
| H | -2.21943409 | -1.38146348 | 0.00000000 |

State=1-A"
<S2>= 1.034647, i.e. 48.3% singlet
UB3LYP/6-31G(d), HF=-302.3265626
Zero-point correction= 0.079299 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.247263
Ziegler-Cramer corrected energy ($2*E(T_0) - E(S_1)$)= -302.234349

## 19 Closed-Shell Singlet $S_2$

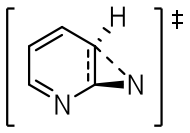
2-Pyridyl-nitrene



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 0.06611052 | 2.38067532 | 0.00000000 |
| N | -1.23703613 | 0.40511059 | 0.00000000 |
| C | 0.00200707 | 1.05903985 | 0.00000000 |
| C | 1.20928569 | 0.28652870 | 0.00000000 |
| C | 1.17964922 | -1.10802840 | 0.00000000 |
| C | -0.07079256 | -1.71111248 | 0.00000000 |
| C | -1.24385502 | -0.90978959 | 0.00000000 |
| H | 2.14029463 | 0.84381116 | 0.00000000 |
| H | 2.09012058 | -1.70114810 | 0.00000000 |
| H | -0.16731936 | -2.79402004 | 0.00000000 |
| H | -2.21719664 | -1.40150702 | 0.00000000 |

State=1-A'"
RB3LYP/6-31G(d), HF=-302.2805444
Zero-point correction= 0.080176 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.200368

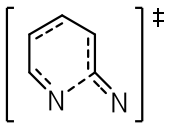
## TS 19 $S_1$ → 20



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 0.15867212 | -1.40100041 | -0.27756331 |
| N | 2.02513230 | -0.01582164 | 0.54288413 |
| C | 1.00367478 | -0.31416689 | -0.13951010 |
| C | 0.58344365 | 1.07182953 | -0.35808724 |
| C | -0.74722417 | 1.31890411 | 0.04565238 |
| C | -1.57480969 | 0.23060243 | 0.26045491 |
| C | -1.09018206 | -1.08958651 | -0.05631110 |
| H | 1.24986031 | 1.81639391 | -0.76510626 |
| H | -1.14518286 | 2.33109654 | 0.05598020 |
| H | -2.62404915 | 0.36004891 | 0.50483823 |
| H | -1.81667432 | -1.89528105 | -0.16615098 |

State=1-A
<S2>= 0.331612, i.e. 83.4% singlet
UB3LYP/6-31G(d), HF= -302.3027122
Zero-point correction= 0.078359 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.224353
Imaginary frequency: -564.9 $cm^{-1}$

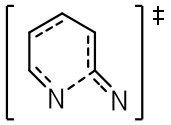
## TS 19 $T_0$ → 23ZZ $T_0$



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 1.50002375 | -0.14741340 | 0.00000000 |
| N | 0.14864618 | -2.44297985 | 0.00000000 |
| C | -0.16905372 | -1.28465128 | 0.00000000 |
| C | -1.28452528 | -0.39478971 | 0.00000000 |
| C | -1.23613759 | 0.98919762 | 0.00000000 |
| C | -0.06051755 | 1.73468323 | 0.00000000 |
| C | 1.23136099 | 1.10864743 | 0.00000000 |
| H | -2.24965159 | -0.89361468 | 0.00000000 |
| H | -2.18459988 | 1.51991567 | 0.00000000 |
| H | -0.10399349 | 2.81878361 | 0.00000000 |
| H | 2.11080141 | 1.76914597 | 0.00000000 |

State=3-A"
<S2>= 2.103161
UB3LYP/6-31G(d), HF= -302.2889592
Zero-point correction= 0.074985 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.213974
Imaginary frequency: -540.0 $cm^{-1}$

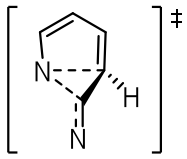
## TS 19 $S_1$ → 23ZZ $S_1$



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -1.50167062 | -0.04699869 | 0.00000000 |
| N | -0.46607723 | 2.40001248 | 0.00000000 |
| C | -0.00912404 | 1.29179022 | 0.00000000 |
| C | 1.21896106 | 0.55725949 | 0.00000000 |
| C | 1.35646873 | -0.82266110 | 0.00000000 |
| C | 0.29228363 | -1.71346167 | 0.00000000 |
| C | -1.07652062 | -1.25096945 | 0.00000000 |
| H | 2.10750631 | 1.18181709 | 0.00000000 |
| H | 2.36750345 | -1.22155187 | 0.00000000 |
| H | 0.47124527 | -2.78331892 | 0.00000000 |
| H | -1.86443255 | -2.01978778 | 0.00000000 |

State=1-A"
<S2>= 1.049555, i.e. 47.5% singlet
UB3LYP/6-31G(d), HF= -302.2814719
Zero-point correction= 0.075184 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.206287
Ziegler-Cramer corrected energy ($2*E(T_0) - E(S_1)$)= -302.221661
Imaginary frequency: -561.3 $cm^{-1}$

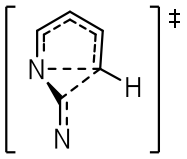
## TS 19 → 32



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -2.29405916 | -0.11705824 | -0.40648067 |
| N | -0.28885384 | -1.25426950 | 0.48236045 |
| C | 0.91130621 | -1.25574608 | 0.00642568 |
| C | 1.66290016 | -0.09444063 | -0.33715388 |
| C | -0.25037990 | 1.26033697 | 0.31975927 |
| C | -1.23536260 | 0.26718600 | -0.00819707 |
| H | 1.35896602 | -2.25113317 | -0.12029677 |
| H | 2.63968260 | -0.18277996 | -0.79844029 |
| H | -0.60805378 | 2.14957435 | 0.83274168 |
| C | 1.07767242 | 1.13181315 | -0.04769118 |
| H | 1.69297847 | 2.02873649 | -0.04401998 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2581948
Zero-point correction= 0.075529 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.182666
Imaginary frequency: -397.1 $cm^{-1}$

## TS 19 → 33

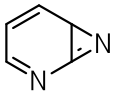


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -0.31713940 | -1.03980709 | 0.54472620 |
| N | -2.22269765 | 0.25570457 | -0.47819807 |
| C | 0.90657820 | -1.20682413 | -0.04468706 |
| C | 1.63930730 | -0.12501221 | -0.44440763 |
| C | 1.03905058 | 1.11294582 | -0.05987819 |
| C | -0.18208585 | 1.08925412 | 0.50129061 |
| C | -1.21582186 | -0.20023907 | -0.02080594 |
| H | 1.29785647 | -2.21987806 | 0.00641666 |
| H | 2.62895448 | -0.20089221 | -0.87587712 |
| H | 1.57019599 | 2.06111561 | -0.11206990 |
| H | -0.84031783 | 1.82762510 | 0.92676264 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2529578
Zero-point correction= 0.076109 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.176849
Imaginary frequency: -591.1 $cm^{-1}$

## 20

2,7-diazabicyclo[4.1.0]hepta-1(7),2,4-triene



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | 1.38639794 | 0.37523811 | 0.45870229 |
| C | 0.49241799 | 1.36024502 | 0.08834737 |
| H | 2.37075441 | 0.64146572 | 0.83150061 |
| H | 0.82448871 | 2.39568335 | 0.02802865 |
| N | -1.74447097 | 0.05603486 | 0.46463902 |
| C | 1.16597714 | -0.99812501 | 0.08219343 |
| H | 2.01370352 | -1.68190135 | 0.09343688 |

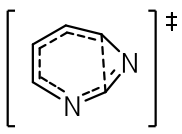
| | | | |
|---|---|---|---|
| N | 0.03167757 | -1.48589010 | -0.38390160 |
| C | -0.89824805 | -0.52083071 | -0.26342261 |
| C | -0.79885969 | 0.97044688 | -0.41917546 |
| H | -1.30550478 | 1.53189319 | -1.19799827 |

State=1-A
RB3LYP/6-31G(d), HF= -302.3194483
Zero-point correction= 0.080211 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.239237

**Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):**

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A | 254.8 | 13.4 | 17 |
| 2 | A | 333.3 | 3.7 | 5 |
| 3 | A | 399.3 | 4.2 | 5 |
| 4 | A | 485.1 | 6.9 | 9 |
| 5 | A | 599.7 | 2.2 | 3 |
| 6 | A | 621.6 | 6.5 | 8 |
| 7 | A | 645.8 | 12.3 | 16 |
| 8 | A | 774.5 | 65.0 | 84 |
| 9 | A | 832.6 | 26.8 | 35 |
| 10 | A | 890.4 | 4.8 | 6 |
| 11 | A | 923.8 | 10.4 | 13 |
| 12 | A | 930.6 | 2.1 | 3 |
| 13 | A | 946.0 | 3.3 | 4 |
| 14 | A | 961.1 | 2.0 | 3 |
| 15 | A | 1003.1 | 16.3 | 21 |
| 16 | A | 1051.2 | 1.4 | 2 |
| 17 | A | 1143.1 | 5.9 | 8 |
| 18 | A | 1261.4 | 11.8 | 15 |
| 19 | A | 1316.3 | 25.9 | 34 |
| 20 | A | 1387.3 | 4.6 | 6 |
| 21 | A | 1435.7 | 61.1 | 79 |
| 22 | A | 1530.3 | 14.8 | 19 |
| 23 | A | 1780.4 | 76.5 | 99 |
| 24 | A | 3044.3 | 4.5 | 6 |
| 25 | A | 3049.3 | 9.6 | 12 |
| 26 | A | 3079.1 | 13.4 | 17 |
| 27 | A | 3085.3 | 8.3 | 11 |

## TS 20 → 21



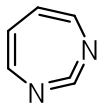

| Atom | Coordinates (Angstroms) | | |
|---|---|---|---|
| Type | X | Y | Z |
| C | 1.16204972 | 0.89819506 | 0.29395498 |
| C | -0.09234758 | 1.42665039 | -0.07731743 |
| H | 1.98027104 | 1.57665921 | 0.51365520 |

| | | | |
|---|---|---|---|
| H | -0.13368411 | 2.46316482 | -0.41132643 |
| N | -1.56084233 | -0.56405595 | 0.61950092 |
| C | 1.48059087 | -0.44305039 | 0.02901654 |
| H | 2.52054580 | -0.76081627 | 0.02198124 |
| N | 0.58359121 | -1.37954653 | -0.36151427 |
| C | -0.60136192 | -0.91969274 | -0.09220573 |
| C | -1.20714956 | 0.61425353 | -0.30405877 |
| H | -1.97706403 | 0.86807450 | -1.02655406 |

State=1-A
RB3LYP/6-31G(d), HF= -302.3175151
Zero-point correction= 0.079105 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.238410
Imaginary frequency: -428.2 $cm^{-1}$

## 21

1,3-diazacyclohepta-1,2,4,6-tetraene




| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 1.14673773 | 1.07112189 | -0.42833708 |
| C | 0.00000560 | 1.22590947 | 0.00000170 |
| C | -1.56579524 | -0.20564742 | -0.11261583 |
| C | -0.71152761 | -1.24616776 | -0.18908760 |
| C | 0.71151578 | -1.24617362 | 0.18908973 |
| C | 1.56579387 | -0.20566232 | 0.11261394 |
| H | -2.60510873 | -0.27088780 | -0.41039144 |
| H | -1.12144314 | -2.19506021 | -0.51901298 |
| H | 1.12142058 | -2.19506713 | 0.51902567 |
| H | 2.60510434 | -0.27090848 | 0.41039871 |
| N | -1.14672891 | 1.07113137 | 0.42833717 |

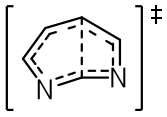
State=1-A
RB3LYP/6-31G(d), HF= -302.336406
Zero-point correction= 0.080348 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.256058

### Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A | 288.0 | 0.5 | 0 |
| 2 | A | 291.7 | 17.0 | 5 |
| 3 | A | 370.4 | 16.7 | 5 |
| 4 | A | 482.3 | 0.2 | 0 |
| 5 | A | 547.8 | 29.3 | 8 |
| 6 | A | 617.6 | 0.8 | 0 |
| 7 | A | 678.3 | 0.7 | 0 |
| 8 | A | 739.5 | 58.7 | 16 |
| 9 | A | 814.1 | 2.3 | 1 |

| | | | | |
|---|---|---|---|---|
| 10 | A | 822.5 | 0.5 | 0 |
| 11 | A | 876.0 | 5.9 | 2 |
| 12 | A | 922.6 | 16.1 | 4 |
| 13 | A | 927.4 | 6.7 | 2 |
| 14 | A | 950.0 | 6.6 | 2 |
| 15 | A | 962.3 | 55.5 | 15 |
| 16 | A | 1155.7 | 0.0 | 0 |
| 17 | A | 1175.3 | 2.5 | 1 |
| 18 | A | 1247.9 | 7.1 | 2 |
| 19 | A | 1298.7 | 24.7 | 7 |
| 20 | A | 1363.6 | 1.7 | 0 |
| 21 | A | 1537.5 | 8.2 | 2 |
| 22 | A | 1576.8 | 0.1 | 0 |
| 23 | A | 1993.1 | 369.0 | 100 |
| 24 | A | 3054.9 | 2.7 | 1 |
| 25 | A | 3064.5 | 2.2 | 1 |
| 26 | A | 3090.8 | 19.8 | 5 |
| 27 | A | 3093.0 | 6.5 | 2 |

## TS 21 → 24

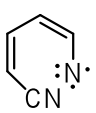


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 1.38351970 | -0.94632933 | -0.27930866 |
| N | -1.03928615 | -1.20540842 | 0.17409713 |
| C | -1.64669786 | 0.02723691 | -0.24204597 |
| C | -0.87887779 | 1.14781031 | -0.20246360 |
| C | 0.46326728 | 1.07538968 | 0.42824294 |
| C | 0.15965456 | -0.89107662 | 0.28645542 |
| C | 1.61261452 | 0.35903126 | -0.08832958 |
| H | -2.66149750 | -0.04703920 | -0.61517849 |
| H | -1.29051818 | 2.10511328 | -0.51599589 |
| H | 0.68379450 | 1.91714527 | 1.09220344 |
| H | 2.59882211 | 0.77659570 | -0.31570366 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2598589
Zero-point correction= 0.077752 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.182107
Imaginary frequency: -791.9 $cm^{-1}$

## 23ZZ $T_0$

*(2Z,3s-Z,4Z)*-5-cyanopenta-2,4-dienenitrene



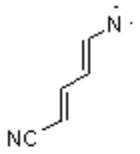
| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 0.46599583 | -1.78048905 | 0.00000000 |
| N | 2.42498206 | 0.63889777 | 0.00000000 |
| C | 1.29985409 | 0.95450387 | 0.00000000 |
| C | 0.00000015 | 1.50768400 | 0.00000000 |
| C | -1.23299392 | 0.87417812 | 0.00000000 |
| C | -1.61137005 | -0.47706584 | 0.00000000 |
| C | -0.80526016 | -1.67436992 | 0.00000000 |
| H | -0.00729575 | 2.59539400 | 0.00000000 |
| H | -2.07360185 | 1.56531020 | 0.00000000 |
| H | -2.68242906 | -0.66107174 | 0.00000000 |
| H | -1.37490625 | -2.61807987 | 0.00000000 |

State= 3-A"
<S2>= 2.070425
UB3LYP/6-31G(d), HF= -302.3033377
Zero-point correction= 0.075266 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.228072

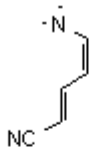
**Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):**

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A" | 16.6 | 1.1 | 2 |
| 2 | A' | 143.3 | 3.1 | 6 |
| 3 | A' | 186.7 | 10.5 | 20 |
| 4 | A" | 191.1 | 13.0 | 24 |
| 5 | A' | 368.9 | 4.4 | 8 |
| 6 | A" | 382.5 | 0.6 | 1 |
| 7 | A" | 515.9 | 1.2 | 2 |
| 8 | A' | 569.6 | 10.9 | 21 |
| 9 | A" | 662.1 | 52.5 | 99 |
| 10 | A" | 767.7 | 1.1 | 2 |
| 11 | A' | 782.5 | 7.7 | 15 |
| 12 | A' | 855.0 | 1.0 | 2 |
| 13 | A" | 867.5 | 0.2 | 0 |
| 14 | A' | 941.3 | 3.5 | 7 |
| 15 | A" | 957.4 | 0.3 | 1 |
| 16 | A' | 1142.3 | 2.5 | 5 |
| 17 | A' | 1214.1 | 3.6 | 7 |
| 18 | A' | 1220.8 | 0.7 | 1 |
| 19 | A' | 1308.4 | 0.6 | 1 |
| 20 | A' | 1412.0 | 2.6 | 5 |
| 21 | A' | 1463.7 | 5.8 | 11 |
| 22 | A' | 1531.1 | 8.2 | 16 |
| 23 | A' | 2185.2 | 0.8 | 1 |
| 24 | A' | 2868.7 | 15.4 | 29 |
| 25 | A' | 3043.5 | 2.9 | 6 |
| 26 | A' | 3060.1 | 0.7 | 1 |
| 27 | A' | 3072.0 | 9.8 | 18 |

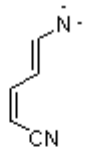
**Natural Atomic Spin Density on Nitrene N for Isomers of 23 $T_0$ (UB3LYP/EPR-III):**



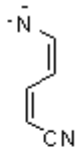
*s-E,E,E*
ρ= 1.2582



*s-E,E,Z*
ρ= 1.2679



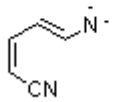
*s-E,Z,E*
ρ= 1.2636



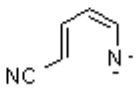
*s-E,Z,Z*
ρ= 1.2713



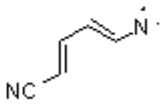
*s-Z,Z,Z*
ρ= 1.2241



*s-Z,Z,E*
ρ= 1.2486



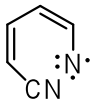
*s-Z,E,Z*
ρ= 1.2106



*s-Z,E,E*
ρ= 1.2272

## 23ZZ $S_1$

*(2Z,3s-Z,4Z)*-5-cyanopenta-2,4-dienenitrene

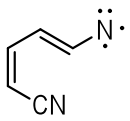


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 2.42621335 | 0.63866327 | 0.00000000 |
| N | 0.46277725 | -1.78416777 | 0.00000000 |
| C | 1.30063623 | 0.95566587 | 0.00000000 |
| C | 0.00357609 | 1.50732413 | 0.00000000 |
| C | -1.23942393 | 0.87095520 | 0.00000000 |
| C | -1.61551069 | -0.46768122 | 0.00000000 |
| C | -0.79683111 | -1.67682615 | 0.00000000 |
| H | -0.00505673 | 2.59494180 | 0.00000000 |
| H | -2.07676621 | 1.56608751 | 0.00000000 |
| H | -2.68512733 | -0.65911593 | 0.00000000 |
| H | -1.37066340 | -2.62000880 | 0.00000000 |

State= 1-A"
<S2>= 1.032388, i.e. 48.3% singlet
UB3LYP/6-31G(d), HF= -302.2970887
Zero-point correction= 0.075129 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.221960
Ziegler-Cramer corrected energy ($2*E(T_0) - E(S_1)$)= -302.234184

## 23EZ $T_0$

*(2E,3s-Z,4Z)*-5-cyanopenta-2,4-dienenitrene



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -0.91326926 | -2.64912592 | 0.00000000 |
| N | 2.50977995 | 0.54858859 | 0.00000000 |
| C | 1.45166724 | 1.04383079 | 0.00000000 |
| C | 0.18851023 | 1.67708430 | 0.00000000 |
| C | -1.04871155 | 1.04770717 | 0.00000000 |
| C | -1.38153230 | -0.31477737 | 0.00000000 |
| C | -0.48557214 | -1.44436641 | 0.00000000 |
| H | 0.21568619 | 2.76319377 | 0.00000000 |
| H | -1.89767623 | 1.72784427 | 0.00000000 |
| H | -2.43906170 | -0.56376738 | 0.00000000 |
| H | 0.59930805 | -1.28038023 | 0.00000000 |

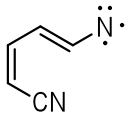
State= 3-A"
<S2>= 2.068785
UB3LYP/6-31G(d), HF= -302.3106982
Zero-point correction= 0.075587 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.235111

**Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):**

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A" | 117.8 | 4.6 | 8 |
| 2 | A' | 126.9 | 4.5 | 7 |
| 3 | A" | 159.4 | 5.6 | 9 |
| 4 | A' | 223.2 | 6.7 | 11 |
| 5 | A" | 358.1 | 0.2 | 0 |
| 6 | A' | 380.4 | 13.7 | 23 |
| 7 | A' | 504.6 | 2.6 | 4 |
| 8 | A" | 508.4 | 2.6 | 4 |
| 9 | A" | 687.3 | 60.0 | 100 |
| 10 | A' | 740.3 | 0.1 | 0 |
| 11 | A" | 806.3 | 6.8 | 11 |
| 12 | A" | 860.1 | 2.8 | 5 |
| 13 | A' | 904.5 | 0.2 | 0 |
| 14 | A" | 961.4 | 0.0 | 0 |
| 15 | A' | 987.1 | 4.9 | 8 |
| 16 | A' | 1132.9 | 0.1 | 0 |
| 17 | A' | 1179.8 | 0.9 | 1 |
| 18 | A' | 1196.2 | 6.8 | 11 |
| 19 | A' | 1347.2 | 4.0 | 7 |
| 20 | A' | 1417.3 | 15.3 | 26 |
| 21 | A' | 1443.2 | 0.4 | 1 |
| 22 | A' | 1493.2 | 2.8 | 5 |
| 23 | A' | 2193.6 | 3.7 | 6 |
| 24 | A' | 2938.2 | 6.2 | 10 |
| 25 | A' | 3052.6 | 3.1 | 5 |
| 26 | A' | 3072.9 | 0.5 | 1 |
| 27 | A' | 3079.2 | 3.5 | 6 |

## 23EZ $S_1$

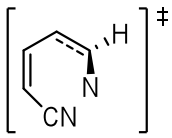
*(2E,3s-Z,4Z)*-5-cyanopenta-2,4-dienenitrene



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -0.90539095 | -2.64437602 | 0.00000000 |
| N | 2.51265205 | 0.54937738 | 0.00000000 |
| C | 1.45265401 | 1.04301763 | 0.00000000 |
| C | 0.19193950 | 1.67366890 | 0.00000000 |
| C | -1.05672874 | 1.04238600 | 0.00000000 |
| C | -1.39041471 | -0.30640682 | 0.00000000 |
| C | -0.48438431 | -1.44965712 | 0.00000000 |
| H | 0.21756003 | 2.75977234 | 0.00000000 |
| H | -1.90131906 | 1.72801056 | 0.00000000 |
| H | -2.44631418 | -0.56045360 | 0.00000000 |
| H | 0.60085096 | -1.28039037 | 0.00000000 |

State= 1-A"
<S2>= 1.031455, i.e. 48.4% singlet
UB3LYP/6-31G(d), HF= -302.3044962
Zero-point correction= 0.075522 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.228974
Ziegler-Cramer corrected energy ($2*E(T_0) - E(S_1)$)= -302.241248

## TS 23ZZ $T_0$ → 23EZ $T_0$

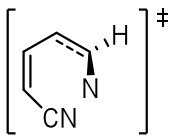


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -1.62094057 | -1.43828377 | -0.62141633 |
| N | 1.97622306 | -1.37002808 | 0.27062202 |
| C | 1.58595376 | -0.29026819 | 0.04950223 |
| C | 1.17993852 | 1.03654553 | -0.19471941 |
| C | -0.13067718 | 1.53139367 | -0.09329802 |
| C | -1.29779565 | 0.84555602 | 0.16556347 |
| C | -1.43755851 | -0.63397777 | 0.32246363 |
| H | 1.97747795 | 1.73210050 | -0.44013240 |
| H | -0.22609908 | 2.60684612 | -0.22841475 |
| H | -2.21946254 | 1.41373228 | 0.27208658 |
| H | -1.41805943 | -1.02999149 | 1.35494939 |

State= 3-A
<S2>= 2.047719
UB3LYP/6-31G(d), HF= -302.2946969
Zero-point correction= 0.074117 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.220580

Imaginary frequency: -169.1 $cm^{-1}$

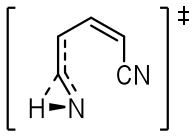
## TS 23ZZ $S_1$ → 23EZ $S_1$



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -1.48781320 | -1.32141835 | -0.63505003 |
| N | 1.98229973 | -1.41074805 | 0.16865732 |
| C | 1.57357826 | -0.33243903 | -0.02244297 |
| C | 1.15902266 | 0.99714901 | -0.23580251 |
| C | -0.13745906 | 1.50779048 | -0.06671557 |
| C | -1.30209812 | 0.85425392 | 0.28338260 |
| C | -1.50199391 | -0.61700312 | 0.40496275 |
| H | 1.94724758 | 1.68782363 | -0.52236176 |
| H | -0.22117894 | 2.58404782 | -0.20330863 |
| H | -2.19969359 | 1.45419835 | 0.42313671 |
| H | -1.73407973 | -1.05941251 | 1.38697688 |

State= 1-A
<S2>= 1.001264, i.e. 49.9% singlet
UB3LYP/6-31G(d), HF= -302.2943865
Zero-point correction= 0.074214 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.220173
Ziegler-Cramer corrected energy ($2*E(T_0) - E(S_1)$)= -302.220987
Imaginary frequency: -113.4 $cm^{-1}$

## TS 23ZZ → 26Z

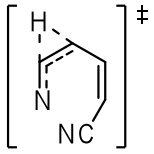


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -0.86334355 | -1.68494301 | 0.35379818 |
| N | 1.50991233 | -1.32890288 | -0.46413996 |
| C | 1.41046420 | -0.21250560 | -0.11564084 |
| C | 1.11993284 | 1.13012385 | 0.19368357 |
| C | -0.16711852 | 1.58941525 | 0.03927470 |
| C | -1.32034417 | 0.79757446 | -0.21925639 |
| C | -1.31185650 | -0.55337881 | 0.09522111 |
| H | 1.92042791 | 1.78018385 | 0.52703057 |
| H | -0.33383802 | 2.65943905 | 0.15342682 |
| H | -2.27318812 | 1.25789073 | -0.44272841 |
| H | -2.22585033 | -1.10796734 | 0.57497064 |

State=1-A
RB3LYP/6-31G(d), HF= -302.253361
Zero-point correction= 0.072522 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.180839
Imaginary frequency: -917.3 $cm^{-1}$

## TS 23ZZ → 27Z

~1,2-H shift

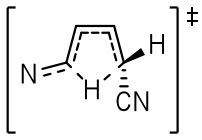



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 1.07504164 | -1.93598793 | -0.35887340 |
| N | 1.87656686 | 0.87400015 | 0.15564686 |
| C | 0.76229643 | 1.35655544 | 0.03772563 |
| C | -0.64671995 | 1.38839385 | -0.30939731 |
| C | -1.54400418 | 0.35930219 | 0.06134895 |
| C | -1.22334678 | -0.95998820 | 0.28462967 |
| C | 0.04487941 | -1.50071452 | -0.01919870 |
| H | 0.59689294 | 2.21148823 | 0.78342123 |
| H | -1.04253835 | 2.37659061 | -0.51599138 |
| H | -2.59042882 | 0.63676432 | 0.17378938 |
| H | -1.97862529 | -1.65036174 | 0.64747613 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2551334
Zero-point correction= 0.073062 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.182071
Imaginary frequency: -374.2 $cm^{-1}$

## TS 23EZ → 27Z

~1,4-H shift

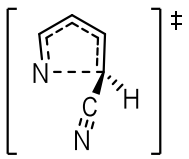



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -2.11823683 | -1.31306177 | -0.11798976 |
| N | 2.18023054 | -1.34576718 | -0.34553963 |
| C | 1.65230310 | -0.37742864 | 0.04171171 |
| C | 1.07070485 | 0.82228204 | 0.51495153 |
| C | -0.01674983 | 1.49254575 | -0.11925201 |

| | | | |
|---|---|---|---|
| C | -1.23168359 | 0.91764599 | -0.34763545 |
| C | -1.36849559 | -0.41992683 | 0.25620267 |
| H | 1.71856039 | 1.40810778 | 1.16622148 |
| H | 0.09364419 | 2.55807127 | -0.32227373 |
| H | -2.01867553 | 1.33230725 | -0.96584957 |
| H | -0.51053353 | -0.53773536 | 1.01680721 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2616385
Zero-point correction= 0.073938 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.187701
Imaginary frequency: -288.0 $cm^{-1}$

## TS 23ZZ $S_1$ → 32

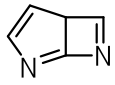



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -2.44685550 | -0.45654217 | -0.56735642 |
| N | 0.52255474 | -1.44495774 | 0.74856948 |
| C | 1.41231570 | -1.04443569 | -0.04975496 |
| C | 1.59355486 | 0.36372308 | -0.44665177 |
| C | 0.66962738 | 1.28733029 | -0.10110981 |
| C | -0.60350796 | 0.97947136 | 0.51729079 |
| C | -1.58753842 | 0.16357670 | -0.07210428 |
| H | 2.10859662 | -1.78633563 | -0.47050581 |
| H | 2.49945898 | 0.63866961 | -0.97895032 |
| H | 0.90587841 | 2.34334641 | -0.23413680 |
| H | -0.95053799 | 1.61682452 | 1.32908165 |

State=1-A
<S2>= 0.824212, i.e. 58.8% singlet
UB3LYP/6-31G(d), HF= -302.2882867
Zero-point correction= 0.074503 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.213784
Imaginary frequency: -252.7 $cm^{-1}$

## 24

2,7-diazabicyclo[3.2.0]hepta-1,3,6-triene




| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 0.79430989 | -1.22145720 | -0.05108063 |

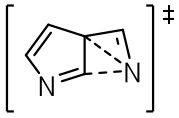
| | | | |
|---|---|---|---|
| N | -1.62793071 | -0.78410219 | -0.09520976 |
| C | -0.27231469 | -0.66129488 | 0.41553150 |
| C | -1.55424423 | 0.49051088 | -0.30127009 |
| C | -0.24815723 | 0.86570536 | 0.46354509 |
| C | 1.10481069 | 1.09149395 | -0.11026860 |
| C | 1.67465873 | -0.14257254 | -0.25494202 |
| H | -2.23302005 | 1.08713586 | -0.90799210 |
| H | -0.47857105 | 1.40289429 | 1.38858346 |
| H | 1.62179440 | 2.04089462 | -0.18001590 |
| H | 2.69662282 | -0.35506567 | -0.55211806 |

State=1-A
RB3LYP/6-31G(d), HF= -302.3074558
Zero-point correction= 0.080397 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.227058

**Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):**

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A | 264.1 | 1.7 | 3 |
| 2 | A | 319.3 | 4.0 | 6 |
| 3 | A | 490.8 | 5.6 | 9 |
| 4 | A | 561.0 | 25.0 | 41 |
| 5 | A | 658.4 | 24.1 | 40 |
| 6 | A | 714.9 | 20.5 | 34 |
| 7 | A | 758.8 | 13.2 | 22 |
| 8 | A | 801.3 | 1.8 | 3 |
| 9 | A | 831.4 | 21.5 | 35 |
| 10 | A | 878.4 | 10.3 | 17 |
| 11 | A | 909.0 | 11.5 | 19 |
| 12 | A | 930.4 | 5.5 | 9 |
| 13 | A | 981.2 | 28.7 | 47 |
| 14 | A | 1025.9 | 29.1 | 48 |
| 15 | A | 1045.4 | 2.5 | 4 |
| 16 | A | 1073.5 | 18.3 | 30 |
| 17 | A | 1115.8 | 16.8 | 27 |
| 18 | A | 1186.1 | 6.3 | 10 |
| 19 | A | 1226.7 | 6.9 | 11 |
| 20 | A | 1306.0 | 18.6 | 30 |
| 21 | A | 1452.5 | 4.0 | 6 |
| 22 | A | 1514.4 | 25.0 | 41 |
| 23 | A | 1551.3 | 60.9 | 100 |
| 24 | A | 2988.3 | 3.7 | 6 |
| 25 | A | 3064.9 | 1.3 | 2 |
| 26 | A | 3096.4 | 6.8 | 11 |
| 27 | A | 3120.2 | 10.8 | 18 |

## TS 24 → 25

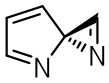


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -1.78354117 | 0.57040360 | 0.43299170 |
| N | 0.56282081 | -1.26223226 | 0.03525266 |
| C | 1.61670243 | -0.47814546 | 0.40407423 |
| C | 1.40453076 | 0.90111080 | 0.24722388 |
| C | 0.15734012 | 1.00795533 | -0.37057548 |
| C | -0.30838546 | -0.40362804 | -0.50368344 |
| C | -1.75633348 | -0.45477363 | -0.29517721 |
| H | 2.53228652 | -0.94898627 | 0.75232856 |
| H | 2.11117487 | 1.69450901 | 0.44930173 |
| H | -0.26256182 | 1.86778020 | -0.87244152 |
| H | -2.51898337 | -1.20561628 | -0.49807110 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2928914
Zero-point correction= 0.078480 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.214412
Imaginary frequency: -284.1 $cm^{-1}$

## 25

1,4-diazaspiro[2.4]hepta-1,4,6-triene




| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 1.84520348 | -0.02518089 | -0.71171468 |
| N | -0.33028274 | -1.18310979 | -0.00261763 |
| C | -1.55695747 | -0.75147755 | 0.01349780 |
| C | -1.67429880 | 0.70892589 | 0.01687689 |
| C | -0.40709331 | 1.18511179 | 0.00553219 |
| C | 0.46327472 | -0.00193851 | 0.02495639 |
| C | 1.83402307 | -0.05221027 | 0.53619983 |
| H | -2.39382583 | -1.44600417 | 0.01767432 |
| H | -2.59927438 | 1.27302136 | 0.01620695 |
| H | -0.06428493 | 2.21195685 | -0.00714444 |
| H | 2.49925065 | -0.11140742 | 1.39121076 |

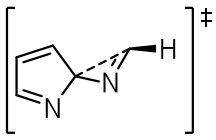
State=1-A
RB3LYP/6-31G(d), HF= -302.3290112
Zero-point correction= 0.079378 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.249633

### Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A | 177.1 | 7.3 | 12 |
| 2 | A | 318.4 | 10.4 | 17 |
| 3 | A | 357.0 | 3.5 | 6 |
| 4 | A | 513.0 | 0.3 | 0 |
| 5 | A | 573.0 | 8.7 | 14 |

| | | | | |
|---|---|---|---|---|
| 6 | A | 619.3 | 4.0 | 7 |
| 7 | A | 715.4 | 12.4 | 20 |
| 8 | A | 772.6 | 16.4 | 27 |
| 9 | A | 784.1 | 35.5 | 58 |
| 10 | A | 839.3 | 5.0 | 8 |
| 11 | A | 859.9 | 25.6 | 42 |
| 12 | A | 895.5 | 5.2 | 9 |
| 13 | A | 925.2 | 1.6 | 3 |
| 14 | A | 962.0 | 8.6 | 14 |
| 15 | A | 1005.6 | 15.8 | 26 |
| 16 | A | 1057.7 | 33.3 | 55 |
| 17 | A | 1138.1 | 23.4 | 38 |
| 18 | A | 1187.8 | 61.0 | 100 |
| 19 | A | 1292.2 | 33.4 | 55 |
| 20 | A | 1333.3 | 1.5 | 2 |
| 21 | A | 1443.6 | 15.0 | 25 |
| 22 | A | 1562.2 | 12.4 | 20 |
| 23 | A | 1721.9 | 43.0 | 71 |
| 24 | A | 3068.6 | 18.6 | 31 |
| 25 | A | 3108.0 | 1.0 | 2 |
| 26 | A | 3110.8 | 4.2 | 7 |
| 27 | A | 3132.9 | 4.0 | 7 |

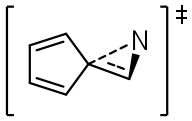
## TS 25 → 36




| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 1.71065824 | -0.54311055 | -0.24260676 |
| N | -0.57016863 | -1.24039539 | -0.07280313 |
| C | 0.33874441 | -0.26643860 | -0.28327072 |
| C | 2.14671859 | 0.47134943 | 0.34336124 |
| C | -0.23515455 | 1.08450895 | -0.18639977 |
| C | -1.55673787 | 0.86397130 | 0.12600016 |
| C | -1.70457571 | -0.56156489 | 0.16402556 |
| H | 2.81954207 | 0.44533128 | 1.20791778 |
| H | 0.25442363 | 1.99778901 | -0.49407278 |
| H | -2.35325264 | 1.59131533 | 0.21397719 |
| H | -2.63810965 | -1.10085111 | 0.29774825 |

State=1-A
RB3LYP/6-31G(d), HF= -302.266671
Zero-point correction= 0.076185 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.190486
Imaginary frequency: -344.4 $cm^{-1}$

## TS 25 → 38 $S_1$

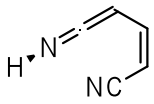


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 2.23162400 | 0.38003758 | -0.68239633 |
| N | -0.36393856 | -1.22908030 | 0.18931151 |
| C | -1.61750757 | -0.83292085 | -0.02188797 |
| C | -1.74941371 | 0.61373085 | -0.17112181 |
| C | -0.48845535 | 1.10720039 | -0.02654097 |
| C | 0.34112970 | -0.06103135 | 0.24934694 |
| C | 1.81072288 | -0.05041583 | 0.41312408 |
| H | -2.42904291 | -1.55481552 | -0.04371900 |
| H | -2.66719245 | 1.15680692 | -0.35544916 |
| H | -0.14039609 | 2.13008766 | -0.06405125 |
| H | 2.38397773 | -0.44815918 | 1.25729151 |

State=1-A
<S2>= 0.626254, i.e. 68.7% singlet
UB3LYP/6-31G(d), HF= -302.3023396
Zero-point correction= 0.076589 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.225750
Imaginary frequency: -267.4 $cm^{-1}$

## 26Z

*(Z)*-5-iminopenta-2,4-dienenitrile



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -1.41302835 | -1.83227414 | 0.15115930 |
| N | 2.04003015 | -1.08259302 | -0.26468533 |
| C | 1.50187319 | -0.03339369 | 0.03550207 |
| C | 0.98222524 | 1.18231408 | 0.20099961 |
| C | -0.40118899 | 1.54254103 | -0.03045007 |
| C | -1.48530625 | 0.73651405 | -0.15428158 |
| C | -1.44256246 | -0.67656639 | -0.00132519 |
| H | 2.05606589 | -1.84685398 | 0.41423839 |
| H | 1.66694944 | 1.95889232 | 0.53145304 |
| H | -0.58233032 | 2.61272962 | -0.09994910 |
| H | -2.45994198 | 1.17084777 | -0.35372918 |

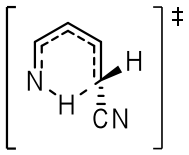
State=1-A
RB3LYP/6-31G(d), HF= -302.3577818
Zero-point correction= 0.077536 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.280245

**Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):**

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A | 70.6 | 10.9 | 2 |
| 2 | A | 104.9 | 3.0 | 1 |
| 3 | A | 174.9 | 4.3 | 1 |
| 4 | A | 322.8 | 6.2 | 1 |
| 5 | A | 383.2 | 2.0 | 0 |
| 6 | A | 433.4 | 71.9 | 14 |
| 7 | A | 509.8 | 20.3 | 4 |
| 8 | A | 569.1 | 2.6 | 0 |
| 9 | A | 622.5 | 17.5 | 3 |
| 10 | A | 724.5 | 41.2 | 8 |
| 11 | A | 769.6 | 8.0 | 2 |
| 12 | A | 812.9 | 60.7 | 12 |
| 13 | A | 892.4 | 125.4 | 24 |
| 14 | A | 905.6 | 234.7 | 45 |
| 15 | A | 949.4 | 9.6 | 2 |
| 16 | A | 968.6 | 16.8 | 3 |
| 17 | A | 1125.1 | 2.5 | 0 |
| 18 | A | 1205.6 | 4.7 | 1 |
| 19 | A | 1369.7 | 9.2 | 2 |
| 20 | A | 1406.3 | 28.8 | 6 |
| 21 | A | 1581.1 | 91.5 | 18 |
| 22 | A | 2051.1 | 520.6 | 100 |
| 23 | A | 2237.1 | 32.0 | 6 |
| 24 | A | 3056.9 | 10.6 | 2 |
| 25 | A | 3068.4 | 0.2 | 0 |
| 26 | A | 3084.3 | 1.8 | 0 |
| 27 | A | 3379.1 | 52.5 | 10 |

## TS 26Z → 27Z

~1,5-H shift

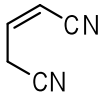


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -2.42873582 | 0.43020185 | -0.52520434 |
| N | 0.60847436 | 1.56817448 | 0.35457026 |
| C | 1.36198279 | 0.90325963 | -0.30409507 |
| C | 1.65255384 | -0.43695883 | -0.55074873 |
| C | 0.68466224 | -1.24627446 | 0.03064128 |
| C | -0.50045884 | -0.80489012 | 0.70084825 |
| C | -1.55330515 | -0.11809076 | 0.01367666 |
| H | 0.16295017 | 0.80476076 | 1.12236628 |
| H | 2.60725528 | -0.80247737 | -0.90178885 |
| H | 0.97341258 | -2.28765537 | 0.16702361 |
| H | -0.87439709 | -1.48553506 | 1.46490318 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2845308
Zero-point correction= 0.073250 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.211280
Imaginary frequency: -964.0 $cm^{-1}$

## 27Z

*(Z)*-pent-2-enedinitrile




| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -2.74527464 | -1.07674195 | -0.27867193 |
| N | 3.09175841 | -0.40174026 | -0.59661532 |
| C | 0.03670779 | 0.99957791 | 0.29175378 |
| C | -1.25016199 | 1.03381954 | -0.08556635 |
| C | 0.79368848 | -0.25106013 | 0.67069402 |
| C | 2.07744872 | -0.34643465 | -0.03619038 |
| C | -2.07162441 | -0.13167817 | -0.19248354 |
| H | 0.58758609 | 1.93496629 | 0.34503976 |
| H | -1.72781566 | 1.98027519 | -0.32388584 |
| H | 0.19775929 | -1.14742124 | 0.46574511 |
| H | 1.00073231 | -0.24379175 | 1.75086655 |

State=1-A
RB3LYP/6-31G(d), HF= -302.3847331
Zero-point correction= 0.078749 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.305984

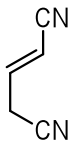
### Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A | 44.1 | 8.7 | 25 |
| 2 | A | 127.0 | 11.5 | 33 |
| 3 | A | 165.8 | 4.1 | 12 |
| 4 | A | 290.7 | 2.2 | 6 |
| 5 | A | 362.8 | 0.5 | 1 |
| 6 | A | 370.3 | 0.3 | 1 |
| 7 | A | 479.0 | 2.8 | 8 |
| 8 | A | 562.8 | 2.9 | 8 |
| 9 | A | 653.3 | 0.6 | 2 |
| 10 | A | 737.6 | 34.6 | 99 |
| 11 | A | 877.2 | 7.0 | 20 |
| 12 | A | 903.8 | 10.3 | 29 |
| 13 | A | 935.2 | 2.2 | 6 |
| 14 | A | 976.9 | 0.5 | 1 |
| 15 | A | 1031.9 | 2.8 | 8 |
| 16 | A | 1187.3 | 1.4 | 4 |
| 17 | A | 1224.4 | 0.4 | 1 |
| 18 | A | 1284.5 | 5.1 | 15 |

| | | | | |
|---|---|---|---|---|
| 19 | A | 1371.6 | 0.1 | 0 |
| 20 | A | 1410.4 | 12.3 | 35 |
| 21 | A | 1635.1 | 7.5 | 21 |
| 22 | A | 2259.7 | 6.8 | 20 |
| 23 | A | 2288.0 | 5.9 | 17 |
| 24 | A | 2922.4 | 0.5 | 2 |
| 25 | A | 2980.7 | 0.4 | 1 |
| 26 | A | 3067.1 | 1.8 | 5 |
| 27 | A | 3083.1 | 0.9 | 3 |

## 27E

*(E)*-pent-2-enedinitrile




| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -1.33215173 | -3.11805475 | 0.00000000 |
| N | -0.40038494 | 2.91635511 | 0.00000000 |
| C | -0.46345150 | -0.67577437 | 0.00000000 |
| C | -0.93282167 | -2.02526612 | 0.00000000 |
| C | 1.41573184 | 1.02068589 | 0.00000000 |
| C | 0.41017577 | 2.08641214 | 0.00000000 |
| C | 0.84256445 | -0.37599810 | 0.00000000 |
| H | -1.22234995 | 0.10374060 | 0.00000000 |
| H | 2.06724895 | 1.15033665 | 0.87590000 |
| H | 2.06724895 | 1.15033665 | -0.87590000 |
| H | 1.58226540 | -1.17291768 | 0.00000000 |

State=1-A'
RB3LYP/6-31G(d), HF= -302.3853781
Zero-point correction= 0.078536 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.306842

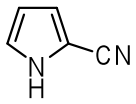
### Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A' | 103.7 | 8.3 | 21 |
| 2 | A" | 116.2 | 7.4 | 19 |
| 3 | A" | 176.8 | 1.2 | 3 |
| 4 | A' | 191.7 | 3.5 | 9 |
| 5 | A" | 361.3 | 0.0 | 0 |
| 6 | A' | 363.0 | 2.9 | 8 |
| 7 | A" | 474.3 | 5.3 | 13 |
| 8 | A' | 515.8 | 0.0 | 0 |
| 9 | A' | 648.0 | 1.2 | 3 |
| 10 | A" | 776.6 | 0.0 | 0 |
| 11 | A' | 843.0 | 0.8 | 2 |
| 12 | A" | 934.4 | 9.2 | 23 |
| 13 | A" | 970.0 | 38.5 | 99 |

| | | | | |
|---|---|---|---|---|
| 14 | A' | 998.2 | 1.9 | 5 |
| 15 | A' | 1010.4 | 7.3 | 19 |
| 16 | A" | 1198.4 | 0.3 | 1 |
| 17 | A' | 1244.3 | 3.0 | 8 |
| 18 | A' | 1292.5 | 0.3 | 1 |
| 19 | A' | 1320.7 | 1.7 | 4 |
| 20 | A' | 1406.6 | 19.4 | 50 |
| 21 | A' | 1647.5 | 13.5 | 35 |
| 22 | A' | 2264.5 | 11.1 | 29 |
| 23 | A' | 2290.2 | 2.9 | 7 |
| 24 | A' | 2924.4 | 1.4 | 4 |
| 25 | A" | 2946.8 | 0.3 | 1 |
| 26 | A' | 3058.5 | 2.0 | 5 |
| 27 | A' | 3069.4 | 1.8 | 5 |

## 28

2-Cyanopyrrole

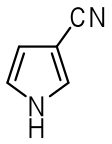



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -1.02609191 | -0.49493102 | 0.00000000 |
| C | 0.06785582 | 0.35341817 | 0.00000000 |
| C | 1.20931687 | -0.43954256 | 0.00000000 |
| C | 0.78592887 | -1.78878129 | 0.00000000 |
| C | -0.59801988 | -1.79090484 | 0.00000000 |
| H | -1.98731309 | -0.18764981 | 0.00000000 |
| H | -1.30318831 | -2.60938827 | 0.00000000 |
| H | 1.41942530 | -2.66464347 | 0.00000000 |
| H | 2.22404632 | -0.06768790 | 0.00000000 |
| C | -0.08049633 | 1.76011718 | 0.00000000 |
| N | -0.21111985 | 2.91829239 | 0.00000000 |

State=1-A'
RB3LYP/6-31G(d), HF= -302.4135317
Zero-point correction= 0.081680 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.331852

## 29

3-Cyanopyrrole

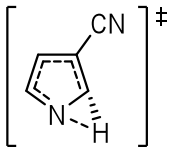



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -1.85499481 | 0.06904919 | 0.00000000 |

| | | | |
|---|---|---|---|
| C | -0.77645541 | 0.90388316 | 0.00000000 |
| C | 0.36235497 | 0.11001783 | 0.00000000 |
| C | -0.06889936 | -1.25748234 | 0.00000000 |
| C | -1.44125697 | -1.24660467 | 0.00000000 |
| H | -2.81674161 | 0.37369913 | 0.00000000 |
| H | -2.15599003 | -2.05606436 | 0.00000000 |
| H | 0.57157102 | -2.12737764 | 0.00000000 |
| H | -0.88021261 | 1.97831758 | 0.00000000 |
| C | 1.70116122 | 0.58513505 | 0.00000000 |
| N | 2.80070146 | 0.96834096 | 0.00000000 |

State=1-A'
RB3LYP/6-31G(d), HF= -302.4146745
Zero-point correction= 0.081744 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.332930

## TS 29 → 35

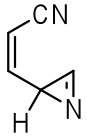



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -0.12791126 | -1.96185430 | -0.07086109 |
| N | -0.84001980 | 2.83167067 | 0.14668503 |
| C | -0.92017612 | -0.76716974 | 0.09095484 |
| C | -0.07903656 | 0.36516011 | 0.00110725 |
| C | 1.22795674 | -0.12340053 | -0.17863898 |
| C | 1.15236198 | -1.51484166 | -0.17253546 |
| C | -0.49458638 | 1.72223779 | 0.08002347 |
| H | -0.63669731 | -1.60808522 | 1.04315482 |
| H | 2.12259946 | 0.47896670 | -0.27151326 |
| H | 1.96675241 | -2.22703635 | -0.20928493 |
| H | -1.99625503 | -0.82447542 | -0.01859095 |

State=1-A
RB3LYP/6-31G(d), HF= -302.3343058
Zero-point correction= 0.076518 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.257787
Imaginary frequency: -1537.9 $cm^{-1}$

## 30

3-(2*H*-aziren-2-yl)acrylonitrile



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 1.68057209 | -0.72100078 | 0.74355700 |
| N | -2.15883785 | -1.14688528 | -0.06492500 |
| C | -1.61735098 | -0.12102221 | 0.04233000 |
| C | -0.98324715 | 1.15420087 | 0.14208100 |
| C | 0.32994682 | 1.36343104 | -0.07923800 |
| C | 1.36375695 | 0.35114518 | -0.36454100 |
| C | 1.12683814 | -1.08811085 | -0.31846800 |
| H | -1.63569926 | 1.98634279 | 0.39170500 |
| H | 0.68253169 | 2.39187809 | -0.02950300 |
| H | 2.25109090 | 0.72770130 | -0.87050300 |
| H | 0.73026626 | -1.98858290 | -0.77510400 |

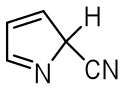
State=1-A
RB3LYP/6-31G(d), HF= -302.3221079
Zero-point correction= 0.077760 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.244347

**Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):**

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A | 64.0 | 12.0 | 22 |
| 2 | A | 123.1 | 6.5 | 12 |
| 3 | A | 223.3 | 13.7 | 25 |
| 4 | A | 276.4 | 1.8 | 3 |
| 5 | A | 368.9 | 5.1 | 10 |
| 6 | A | 481.2 | 0.4 | 1 |
| 7 | A | 566.0 | 1.3 | 2 |
| 8 | A | 667.8 | 1.9 | 3 |
| 9 | A | 743.7 | 4.5 | 8 |
| 10 | A | 759.1 | 53.9 | 100 |
| 11 | A | 783.8 | 11.6 | 22 |
| 12 | A | 883.4 | 7.8 | 14 |
| 13 | A | 928.9 | 7.4 | 14 |
| 14 | A | 965.6 | 4.2 | 8 |
| 15 | A | 972.9 | 25.6 | 47 |
| 16 | A | 1032.2 | 7.7 | 14 |
| 17 | A | 1176.4 | 4.9 | 9 |
| 18 | A | 1237.4 | 18.8 | 35 |
| 19 | A | 1344.8 | 6.0 | 11 |
| 20 | A | 1377.4 | 1.5 | 3 |
| 21 | A | 1612.2 | 14.2 | 26 |
| 22 | A | 1700.0 | 17.2 | 32 |
| 23 | A | 2247.0 | 14.4 | 27 |
| 24 | A | 3032.4 | 17.5 | 32 |
| 25 | A | 3054.1 | 9.1 | 17 |
| 26 | A | 3076.4 | 2.7 | 5 |
| 27 | A | 3107.7 | 2.0 | 4 |

## 32

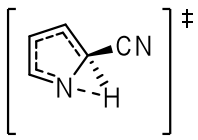
2*H*-Pyrrole-2-carbonitrile




| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 2.69505120 | -0.04775579 | -0.51726051 |
| N | -0.49152203 | -1.20707972 | 0.21088345 |
| C | 1.64305047 | -0.05706339 | -0.02846525 |
| C | 0.31207098 | -0.02921024 | 0.59385603 |
| C | -1.59161649 | -0.72854824 | -0.26167696 |
| C | -1.66350216 | 0.74130753 | -0.29029630 |
| C | -0.50263791 | 1.19162631 | 0.21285573 |
| H | 0.44836190 | -0.06981562 | 1.68612542 |
| H | -2.38348794 | -1.39437526 | -0.59976625 |
| H | -2.50206543 | 1.32599877 | -0.64974369 |
| H | -0.17170209 | 2.21336891 | 0.35038433 |

State=1-A
RB3LYP/6-31G(d), HF= -302.3771838
Zero-point correction= 0.080448 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.296736

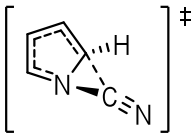
## TS 32 → 28




| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 0.49202235 | -1.17360858 | -0.03205273 |
| N | -2.90891451 | -0.06284612 | -0.11984643 |
| C | -1.75324931 | -0.04007186 | 0.00463349 |
| C | -0.33524822 | 0.02642950 | 0.18059121 |
| C | 0.48631979 | 1.17893068 | 0.09791841 |
| C | 1.78229492 | 0.72664521 | -0.11106392 |
| C | 1.74189885 | -0.67733707 | -0.14222020 |
| H | -0.00474029 | -0.80947931 | 1.10457915 |
| H | 0.14206873 | 2.20107571 | 0.18128631 |
| H | 2.67099069 | 1.33984780 | -0.19748119 |
| H | 2.57782991 | -1.36384004 | -0.20424404 |

State=1-A
RB3LYP/6-31G(d), HF= -302.3272717
Zero-point correction= 0.076248 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.251024
Imaginary frequency: -1526.0 $cm^{-1}$

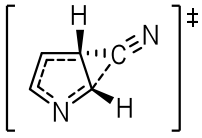
## TS 32 → 33



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -0.17644098 | -0.61003501 | 0.79658100 |
| N | -2.35541800 | -0.04211509 | -0.64986100 |
| C | -1.33330800 | 0.02522595 | -0.06948800 |
| C | 0.83822905 | -1.15717597 | 0.06469200 |
| C | 1.65890201 | -0.17251494 | -0.49401500 |
| C | 1.10559296 | 1.07201304 | -0.19978300 |
| C | -0.05513403 | 0.83394200 | 0.58021600 |
| H | 0.87722709 | -2.22993097 | -0.07420200 |
| H | 2.55035801 | -0.35646590 | -1.08149000 |
| H | 1.48098092 | 2.04393406 | -0.49139600 |
| H | -0.47124306 | 1.49856898 | 1.33031400 |

State=1-A
RB3LYP/6-31G(d), HF= -302.3102016
Zero-point correction= 0.078532 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.231670
Imaginary frequency: -649.0 $cm^{-1}$

## TS 32 → 34

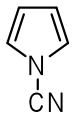


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 2.31814050 | 0.01231762 | -0.71917506 |
| N | -0.97159190 | -1.17662007 | -0.09979354 |
| C | 1.30192704 | -0.00217530 | -0.13473610 |
| C | -0.99835176 | 1.12884269 | -0.06961317 |
| C | -1.57830338 | -0.05313838 | -0.53472391 |
| C | 0.04750736 | -0.76370915 | 0.70351829 |
| C | 0.08190652 | 0.73139356 | 0.76433456 |
| H | -1.25710452 | 2.14393044 | -0.33834196 |
| H | -2.41949250 | -0.12860560 | -1.21650807 |
| H | 0.53457982 | -1.43932627 | 1.39870559 |
| H | 0.58806232 | 1.32683805 | 1.51624673 |

State=1-A
RB3LYP/6-31G(d), HF= -302.3190747
Zero-point correction= 0.078598 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.240477
Imaginary frequency: -698.7 $cm^{-1}$

## 33

1-Cyanopyrrole

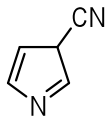



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 0.000000 | 0.000000 | 0.336268 |
| N | 0.000000 | 0.000000 | 2.844348 |
| C | 0.000000 | 0.000000 | 1.679578 |
| C | 0.000000 | 1.140237 | -0.475790 |
| C | 0.000000 | 0.717407 | -1.774380 |
| C | 0.000000 | -0.717407 | -1.774380 |
| C | 0.000000 | -1.140237 | -0.475790 |
| H | 0.000000 | 2.121431 | -0.026187 |
| H | 0.000000 | 1.360337 | -2.643681 |
| H | 0.000000 | -1.360337 | -2.643681 |
| H | 0.000000 | -2.121431 | -0.026187 |

State=1-A1
RB3LYP/6-31G(d), HF= -302.3900591
Zero-point correction= 0.080896 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.309163

## 34

3*H*-Pyrrole-3-carbonitrile

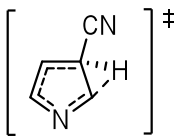



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 1.67920095 | -0.78302147 | -0.31033166 |
| N | -2.72940984 | 0.00542038 | -0.47445771 |
| C | 0.54582835 | -1.15086625 | 0.16538979 |
| C | -1.66976502 | 0.01507330 | -0.00062091 |
| C | -0.33305759 | 0.02164604 | 0.59678691 |
| C | 0.55376714 | 1.17888648 | 0.18876918 |
| C | 1.68424941 | 0.64584123 | -0.30119873 |
| H | 0.25749495 | -2.19281580 | 0.27164314 |
| H | -0.44576707 | -0.01110413 | 1.69356211 |
| H | 0.29130112 | 2.22169945 | 0.30373932 |
| H | 2.56229950 | 1.16194330 | -0.67017644 |

State=1-A
RB3LYP/6-31G(d), HF= -302.3739672

Zero-point correction= 0.080129 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.293838

## TS 34 → 35

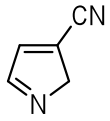



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 1.83516404 | -0.70937245 | -0.10904989 |
| N | -2.93574334 | -0.01290344 | -0.08065802 |
| C | 1.79660901 | 0.64613130 | -0.08060331 |
| C | 0.51610794 | 1.17049281 | 0.04749893 |
| C | -0.35225251 | 0.04515297 | 0.10093133 |
| C | 0.56494524 | -1.12832238 | -0.02132726 |
| C | -1.77653048 | 0.01624208 | 0.00492363 |
| H | 2.72227426 | 1.21048651 | -0.11142350 |
| H | 0.21694878 | 2.20502972 | 0.13813080 |
| H | 0.25199302 | -2.16063857 | -0.12553209 |
| H | 0.01956390 | -0.69712706 | 1.11824023 |

State=1-A
RB3LYP/6-31G(d), HF= -302.3369597
Zero-point correction= 0.076729 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.260231
Imaginary frequency: -1220.3 $cm^{-1}$

## 35

2*H*-Pyrrole-3-carbonitrile

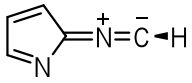



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 0.17701849 | -1.99325939 | 0.00000000 |
| N | 0.71409813 | 2.86110929 | 0.00000000 |
| C | -1.05621093 | -1.61044380 | 0.00000000 |
| C | -1.23419223 | -0.15600056 | 0.00000000 |
| C | 0.01254280 | 0.37565277 | 0.00000000 |
| C | 0.98631429 | -0.78330934 | 0.00000000 |
| C | 0.37835459 | 1.74579502 | 0.00000000 |
| H | -1.87065273 | -2.33167087 | 0.00000000 |
| H | -2.17589732 | 0.37915518 | 0.00000000 |
| H | 1.64394130 | -0.77629910 | 0.87999287 |
| H | 1.64394130 | -0.77629910 | -0.87999287 |

State=1-A'
RB3LYP/6-31G(d), HF= -302.3912314
Zero-point correction= 0.080583 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.310649

## 36

*N*-(2*H*-pyrrol-2-ylidene)methanideiminium



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -0.09531086 | 1.59134878 | -0.01455154 |
| N | -1.15061855 | -0.51139729 | -0.00037571 |
| C | -0.66802945 | -1.73717172 | -0.00402836 |
| C | 0.78006304 | -1.79070271 | -0.00610488 |
| C | 1.20741957 | -0.49069662 | -0.00388355 |
| C | -0.00961881 | 0.28727703 | 0.00050678 |
| C | -0.19198956 | 2.77590786 | 0.13724725 |
| H | -1.33775957 | -2.59209838 | -0.00364462 |
| H | 1.39122154 | -2.68468261 | -0.00730208 |
| H | 2.21635240 | -0.10049111 | -0.00221337 |
| H | -0.25537728 | 3.54992864 | -0.62477259 |

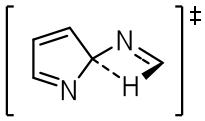
State=1-A
RB3LYP/6-31G(d), HF= -302.3325122
Zero-point correction= 0.078900 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.253612

### Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A | 160.9 | 7.7 | 1 |
| 2 | A | 173.0 | 3.3 | 0 |
| 3 | A | 452.1 | 52.4 | 5 |
| 4 | A | 522.3 | 8.2 | 1 |
| 5 | A | 556.1 | 9.3 | 1 |
| 6 | A | 586.6 | 161.0 | 17 |
| 7 | A | 628.3 | 33.1 | 3 |
| 8 | A | 651.6 | 971.5 | 100 |
| 9 | A | 724.2 | 65.6 | 7 |
| 10 | A | 761.2 | 24.6 | 3 |
| 11 | A | 846.5 | 3.8 | 0 |
| 12 | A | 855.5 | 3.2 | 0 |
| 13 | A | 889.0 | 2.3 | 0 |
| 14 | A | 902.2 | 22.7 | 2 |
| 15 | A | 993.5 | 6.7 | 1 |
| 16 | A | 1043.6 | 14.3 | 1 |
| 17 | A | 1178.9 | 25.0 | 3 |
| 18 | A | 1250.2 | 3.4 | 0 |
| 19 | A | 1317.9 | 7.9 | 1 |

| | | | | |
|---|---|---|---|---|
| 20 | A | 1375.9 | 118.3 | 12 |
| 21 | A | 1404.8 | 0.0 | 0 |
| 22 | A | 1508.6 | 14.3 | 1 |
| 23 | A | 1996.7 | 642.4 | 66 |
| 24 | A | 3084.2 | 13.4 | 1 |
| 25 | A | 3090.4 | 19.3 | 2 |
| 26 | A | 3116.5 | 5.5 | 1 |
| 27 | A | 3137.1 | 5.3 | 1 |

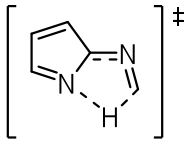
## TS 36 → 40



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 0.32186877 | -1.18439918 | 0.00306896 |
| N | -1.76721710 | -0.01675998 | -0.66270606 |
| C | 1.55346822 | -0.75200554 | 0.00196139 |
| C | 1.67114475 | 0.70500367 | 0.01419497 |
| C | 0.40333981 | 1.18796047 | 0.03133150 |
| C | -0.45212767 | -0.00515446 | -0.00249989 |
| C | -2.12245087 | -0.06652497 | 0.54102183 |
| H | 2.38563048 | -1.45071938 | 0.00205757 |
| H | 2.59538308 | 1.26949945 | 0.01161675 |
| H | 0.05164053 | 2.21087733 | 0.02803210 |
| H | -1.12393101 | -0.04344741 | 1.27547188 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2623327
Zero-point correction= 0.074796 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.187537
Imaginary frequency: -910.4 $cm^{-1}$

## TS 36 → 41



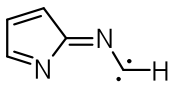
| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 0.00515648 | -0.98192386 | -0.29173711 |
| N | 1.75207671 | 0.65656823 | -0.19154071 |
| C | -1.28335993 | -1.03977456 | 0.04010231 |
| C | -1.80392432 | 0.27190616 | 0.21173880 |
| C | -0.75253992 | 1.18714099 | 0.04645546 |
| C | 0.34671239 | 0.40004234 | -0.27228514 |

| | | | |
|---|---|---|---|
| C | 2.11656088 | -0.35068656 | 0.42705752 |
| H | -1.84026504 | -1.96789184 | -0.00634115 |
| H | -2.85765400 | 0.51589730 | 0.28897362 |
| H | -0.77660151 | 2.26313273 | 0.14150289 |
| H | 1.43319361 | -1.34541896 | 0.24039563 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2537488
Zero-point correction= 0.073945 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.179804
Imaginary frequency: -1093.2 $cm^{-1}$

## 37Z $T_0$

*(s-E,Z)*-2*H*-pyrrol-2-imine-*N*-carbene

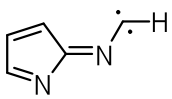


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -0.88802874 | -0.70923908 | 0.00000000 |
| N | -0.34103712 | 1.65855542 | 0.00000000 |
| C | -0.12330593 | -1.78369971 | 0.00000000 |
| C | 1.31387312 | -1.47405655 | 0.00000000 |
| C | 1.38925089 | -0.11451271 | 0.00000000 |
| C | 0.01177473 | 0.34182353 | 0.00000000 |
| C | -1.50781241 | 2.13003199 | 0.00000000 |
| H | -0.55765973 | -2.77961735 | 0.00000000 |
| H | 2.12265780 | -2.19375862 | 0.00000000 |
| H | 2.26058767 | 0.52574631 | 0.00000000 |
| H | -1.72480705 | 3.20489595 | 0.00000000 |

State= 3-A"
<S2>= 2.026165
UB3LYP/6-31G(d), HF= -302.2935162
Zero-point correction= 0.076977 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.216539

## 37E $T_0$

*(s-E,E)*-2*H*-pyrrol-2-imine-*N*-carbene



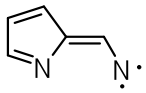
| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 1.34698561 | 0.17744600 | 0.00000000 |
| N | -0.53235191 | 1.61349232 | 0.00000000 |
| C | 1.50745102 | -1.14086993 | 0.00000000 |
| C | 0.23884892 | -1.87541940 | 0.00000000 |

| | | | |
|---|---|---|---|
| C | -0.73062605 | -0.92376286 | 0.00000000 |
| C | -0.00692608 | 0.35086865 | 0.00000000 |
| C | -1.74565647 | 1.93245818 | 0.00000000 |
| H | 2.49978337 | -1.58178604 | 0.00000000 |
| H | 0.12376404 | -2.95212135 | 0.00000000 |
| H | -1.80648438 | -1.03301510 | 0.00000000 |
| H | -2.09804698 | 2.97070635 | 0.00000000 |

State= 3-A"
<S2>= 2.026724
UB3LYP/6-31G(d), HF= -302.2933804
Zero-point correction= 0.076932 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.216448

## 38Z $T_0$

*Z*-(2*H*-pyrrol-2-ylidene)methylnitrene



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | -0.15998644 | -1.78276962 | 0.00000000 |
| C | 1.28673976 | -1.50475093 | 0.00000000 |
| C | 1.39321790 | -0.14811119 | 0.00000000 |
| C | 0.02504962 | 0.34308291 | 0.00000000 |
| N | -0.89533390 | -0.69146022 | 0.00000000 |
| H | -0.61718198 | -2.76827775 | 0.00000000 |
| H | 2.08008409 | -2.24162504 | 0.00000000 |
| H | 2.28899275 | 0.45937818 | 0.00000000 |
| C | -0.36723059 | 1.72718856 | 0.00000000 |
| N | -1.57074781 | 2.15878855 | 0.00000000 |
| H | 0.44393562 | 2.47138793 | 0.00000000 |

State= 3-A"
<S2>= 2.048598
UB3LYP/6-31G(d), HF= -302.3128187
Zero-point correction= 0.077091 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.235728

### Natural Atomic Spin Densities (UB3LYP/EPR-III)

| | | |
|---|---|---|
| 1 | C | 0.31571 |
| 2 | C | 0.19189 |
| 3 | C | -0.02393 |
| 4 | C | 0.50528 |
| 5 | N | -0.09861 |
| 6 | H | -0.00969 |
| 7 | H | -0.00507 |
| 8 | H | -0.00011 |
| 9 | C | -0.23877 |
| 10 | N | 1.27086 |

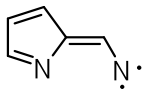
```
    11  H    0.09245
```

**Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):**

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A" | 127.5 | 0.2 | 0 |
| 2 | A' | 206.0 | 2.9 | 6 |
| 3 | A" | 247.0 | 15.0 | 29 |
| 4 | A' | 449.4 | 6.3 | 12 |
| 5 | A" | 521.4 | 3.2 | 6 |
| 6 | A" | 636.6 | 2.4 | 5 |
| 7 | A' | 696.5 | 29.2 | 56 |
| 8 | A" | 724.1 | 51.6 | 99 |
| 9 | A' | 760.2 | 3.3 | 6 |
| 10 | A" | 835.3 | 2.6 | 5 |
| 11 | A" | 845.6 | 13.4 | 26 |
| 12 | A" | 892.5 | 1.7 | 3 |
| 13 | A' | 893.7 | 15.4 | 30 |
| 14 | A' | 945.1 | 7.4 | 14 |
| 15 | A' | 1028.9 | 0.9 | 2 |
| 16 | A' | 1072.4 | 21.5 | 41 |
| 17 | A' | 1162.4 | 1.6 | 3 |
| 18 | A' | 1216.4 | 7.5 | 14 |
| 19 | A' | 1289.6 | 18.8 | 36 |
| 20 | A' | 1335.8 | 48.8 | 94 |
| 21 | A' | 1405.5 | 12.5 | 24 |
| 22 | A' | 1444.8 | 7.3 | 14 |
| 23 | A' | 1510.7 | 8.9 | 17 |
| 24 | A' | 2896.4 | 8.9 | 17 |
| 25 | A' | 3085.0 | 10.7 | 21 |
| 26 | A' | 3118.2 | 3.2 | 6 |
| 27 | A' | 3137.1 | 2.4 | 5 |

## 38Z $S_1$

*Z*-(2*H*-pyrrol-2-ylidene)methylnitrene

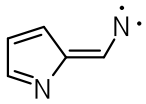



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | -0.15632289 | -1.78815881 | 0.00000000 |
| C | 1.28830339 | -1.50872714 | 0.00000000 |
| C | 1.39126294 | -0.15062485 | 0.00000000 |
| C | 0.02146216 | 0.33419344 | 0.00000000 |
| N | -0.89411587 | -0.68957648 | 0.00000000 |
| H | -0.61612506 | -2.77209126 | 0.00000000 |
| H | 2.08280182 | -2.24407108 | 0.00000000 |
| H | 2.28514512 | 0.45951693 | 0.00000000 |
| C | -0.37503644 | 1.73662465 | 0.00000000 |
| N | -1.56484365 | 2.16687331 | 0.00000000 |
| H | 0.44287987 | 2.47572396 | 0.00000000 |

State= 1-A"
<S2>= 1.01651, i.e. 49.2% singlet
UB3LYP/6-31G(d), HF= -302.305986
Zero-point correction= 0.076739 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.229247

## 38E $T_0$

*E*-(2*H*-pyrrol-2-ylidene)methylnitrene



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | 1.45133179 | -1.21375482 | 0.00000000 |
| C | 0.14780544 | -1.88749221 | 0.00000000 |
| C | -0.77633350 | -0.89143248 | 0.00000000 |
| C | -0.00068648 | 0.34686476 | 0.00000000 |
| N | 1.35085743 | 0.10917785 | 0.00000000 |
| H | 2.42231089 | -1.70053083 | 0.00000000 |
| H | -0.01836479 | -2.95724054 | 0.00000000 |
| H | -1.85563850 | -0.96082555 | 0.00000000 |
| C | -0.50244943 | 1.69759376 | 0.00000000 |
| N | -1.74011188 | 2.00747048 | 0.00000000 |
| H | 0.25846666 | 2.49138452 | 0.00000000 |

State= 3-A"
<S2>= 2.047422
UB3LYP/6-31G(d), HF= -302.3173317
Zero-point correction= 0.077125 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.240207

### Natural Atomic Spin Densities (UB3LYP/EPR-III)

| | | |
|---|---|---|
| 1 | C | 0.38886 |
| 2 | C | 0.09931 |
| 3 | C | 0.04415 |
| 4 | C | 0.49874 |
| 5 | N | -0.12106 |
| 6 | H | -0.01122 |
| 7 | H | -0.00319 |
| 8 | H | -0.00238 |
| 9 | C | -0.22830 |
| 10 | N | 1.24288 |
| 11 | H | 0.09221 |

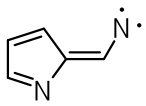
### Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A" | 142.0 | 2.1 | 4 |

| | | | | |
|---|---|---|---|---|
| 2 | A' | 205.4 | 13.2 | 26 |
| 3 | A" | 246.9 | 19.6 | 39 |
| 4 | A' | 475.0 | 4.8 | 10 |
| 5 | A" | 523.4 | 9.7 | 19 |
| 6 | A" | 621.5 | 2.0 | 4 |
| 7 | A' | 628.3 | 19.2 | 38 |
| 8 | A" | 737.6 | 50.1 | 100 |
| 9 | A' | 790.3 | 11.6 | 23 |
| 10 | A" | 837.1 | 0.1 | 0 |
| 11 | A" | 855.8 | 14.1 | 28 |
| 12 | A' | 891.0 | 5.9 | 12 |
| 13 | A" | 899.6 | 0.7 | 1 |
| 14 | A' | 948.5 | 1.8 | 4 |
| 15 | A' | 1041.6 | 14.6 | 29 |
| 16 | A' | 1059.1 | 17.7 | 35 |
| 17 | A' | 1155.6 | 11.9 | 24 |
| 18 | A' | 1193.5 | 11.3 | 23 |
| 19 | A' | 1285.3 | 10.9 | 22 |
| 20 | A' | 1327.7 | 29.9 | 60 |
| 21 | A' | 1373.4 | 31.4 | 63 |
| 22 | A' | 1485.8 | 9.9 | 20 |
| 23 | A' | 1515.3 | 1.2 | 2 |
| 24 | A' | 2912.5 | 4.5 | 9 |
| 25 | A' | 3088.8 | 10.4 | 21 |
| 26 | A' | 3124.2 | 3.0 | 6 |
| 27 | A' | 3146.2 | 1.0 | 2 |

## 38E $S_1$

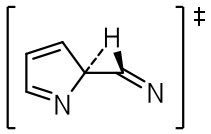
*E*-(2*H*-pyrrol-2-ylidene)methylnitrene



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | 1.44790667 | -1.22208462 | 0.00000000 |
| C | 0.15066992 | -1.89398807 | 0.00000000 |
| C | -0.77369748 | -0.89604846 | 0.00000000 |
| C | 0.00573476 | 0.34290915 | 0.00000000 |
| N | 1.34210545 | 0.11424817 | 0.00000000 |
| H | 2.42169614 | -1.70246568 | 0.00000000 |
| H | -0.01459532 | -2.96357261 | 0.00000000 |
| H | -1.85324352 | -0.96223985 | 0.00000000 |
| C | -0.50812318 | 1.70829478 | 0.00000000 |
| N | -1.73424066 | 2.01330852 | 0.00000000 |
| H | 0.25614511 | 2.50088463 | 0.00000000 |

State= 1-A"
<S2>= 1.016145, 49.2% singlet
UB3LYP/6-31G(d), HF= -302.3109781
Zero-point correction= 0.076798 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.234181

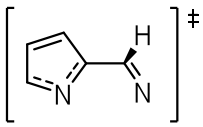
## TS 38 $S_1$ → 32



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | -1.77942039 | 0.83567452 | 0.02001566 |
| C | -1.77464716 | -0.61701564 | -0.07364089 |
| C | 0.26476213 | -0.02943648 | -0.03062196 |
| H | -2.65180934 | 1.47668377 | 0.00773290 |
| H | -2.64791476 | -1.25640364 | -0.15725204 |
| C | 1.70814678 | -0.17345536 | 0.06112471 |
| H | 1.37413175 | -0.26042399 | 1.19753606 |
| C | -0.46826980 | 1.21306009 | 0.10700400 |
| H | -0.04176029 | 2.20474014 | 0.16975070 |
| N | 2.88364134 | -0.22447399 | -0.19220327 |
| N | -0.56022374 | -1.13803445 | -0.05366198 |

State= 1-A
<S2>= 0.316581, i.e. 84.2% singlet
UB3LYP/6-31G(d), HF= 0.073282
Zero-point correction= 0.073282 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.200473
Imaginary frequency: -1320.7 $cm^{-1}$

## TS 38Z $T_0$ → 38E $T_0$

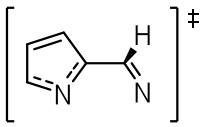


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | -1.69371632 | -0.74605925 | -0.10218537 |
| C | -1.81924309 | 0.70869750 | -0.11030357 |
| C | -0.55260486 | 1.18009792 | 0.05890139 |
| C | 0.28593821 | -0.01505211 | 0.15194927 |
| N | -0.42483129 | -1.15839907 | 0.06029652 |
| H | -2.49966488 | -1.46476999 | -0.21382222 |
| H | -2.73486310 | 1.27240674 | -0.23423145 |
| H | -0.20709814 | 2.20447361 | 0.10143651 |
| C | 1.76314371 | -0.02414353 | 0.37023770 |
| N | 2.63145490 | -0.07997284 | -0.53019051 |
| H | 2.09415495 | 0.03524983 | 1.42427862 |

State= 3-A
<S2>= 2.027119
UB3LYP/6-31G(d), HF= -302.2994816

Zero-point correction= 0.075828 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.223654
Imaginary frequency: -175.2 $cm^{-1}$

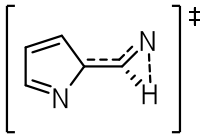
## TS 38Z $S_1$ → 38E $S_1$



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | -1.65667539 | -0.72878889 | -0.14736648 |
| C | -1.79089878 | 0.72800983 | -0.11788510 |
| C | -0.53122651 | 1.20163850 | 0.09062229 |
| C | 0.30471203 | 0.00977204 | 0.21035558 |
| N | -0.39601976 | -1.13793363 | 0.03112994 |
| H | -2.45926445 | -1.44672268 | -0.28584896 |
| H | -2.70774339 | 1.28999799 | -0.24215287 |
| H | -0.19484307 | 2.22655904 | 0.17362161 |
| C | 1.77827087 | 0.00260091 | 0.43366215 |
| N | 2.47043105 | -0.23058965 | -0.58521526 |
| H | 2.21587849 | 0.23043441 | 1.41664678 |

State= 1-A
<S2>= 0.921561, i.e. 53.9% singlet
UB3LYP/6-31G(d), HF= -302.2994774
Zero-point correction= 0.075911 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.223567
Ziegler-Cramer corrected energy ($2*E(T_0) - E(S_1)$)= -302.223741
Imaginary frequency: -127.8 $cm^{-1}$

## TS 38 → 39



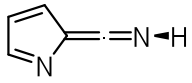
| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | -1.75536932 | -0.67987438 | -0.02934589 |
| C | -1.80856390 | 0.75936192 | -0.16676749 |
| C | -0.50609554 | 1.20053370 | -0.12972480 |
| C | 0.25979756 | 0.01093608 | 0.09687121 |
| H | -2.60528088 | -1.35505450 | -0.01554514 |
| H | -2.70259228 | 1.36646211 | -0.24090550 |
| H | -0.12769185 | 2.21181499 | -0.19130903 |
| C | 1.66076008 | -0.13198119 | 0.05836677 |
| H | 1.90244191 | -0.95275779 | -0.71322480 |

| | | | |
|---|---|---|---|
| N | 2.87282482 | -0.03313294 | 0.21601229 |
| N | -0.52568914 | -1.14177015 | 0.09607138 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2648026
Zero-point correction= 0.073856 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.190947
Imaginary frequency: -823.9 $cm^{-1}$

## 39

(2*H*-pyrrol-2-ylidene)methanimine



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | -1.74169923 | -0.75380311 | 0.01624970 |
| C | -1.86197441 | 0.69052864 | 0.02211405 |
| C | -0.58724481 | 1.17906919 | 0.00803566 |
| C | 0.26238220 | 0.00108234 | -0.00996885 |
| N | -0.50100291 | -1.18303817 | 0.00015046 |
| H | -2.56612760 | -1.46135136 | 0.02494342 |
| H | -2.78313822 | 1.26016545 | 0.03232674 |
| H | -0.25397332 | 2.20846876 | 0.00258591 |
| C | 1.60170795 | -0.02392539 | -0.00519238 |
| N | 2.80772237 | -0.03269253 | -0.13346237 |
| H | 3.41717271 | -0.05487794 | 0.68589828 |

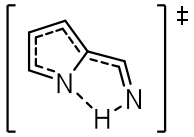
State=1-A
RB3LYP/6-31G(d), HF= -302.3635295
Zero-point correction= 0.079731 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.283799

### Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A | 141.0 | 6.9 | 1 |
| 2 | A | 160.0 | 1.2 | 0 |
| 3 | A | 449.0 | 37.6 | 4 |
| 4 | A | 549.5 | 20.3 | 2 |
| 5 | A | 566.4 | 2.9 | 0 |
| 6 | A | 589.7 | 0.5 | 0 |
| 7 | A | 621.9 | 15.5 | 2 |
| 8 | A | 705.6 | 68.4 | 8 |
| 9 | A | 738.8 | 57.5 | 6 |
| 10 | A | 847.9 | 568.2 | 64 |
| 11 | A | 859.4 | 26.6 | 3 |
| 12 | A | 861.8 | 64.4 | 7 |
| 13 | A | 891.6 | 10.9 | 1 |
| 14 | A | 898.9 | 2.7 | 0 |
| 15 | A | 990.2 | 2.1 | 0 |
| 16 | A | 1049.0 | 14.5 | 2 |

| | | | | |
|---|---|---|---|---|
| 17 | A | 1145.4 | 14.1 | 2 |
| 18 | A | 1239.7 | 0.6 | 0 |
| 19 | A | 1316.0 | 5.6 | 1 |
| 20 | A | 1386.5 | 1.7 | 0 |
| 21 | A | 1389.8 | 77.1 | 9 |
| 22 | A | 1518.4 | 9.2 | 1 |
| 23 | A | 2064.3 | 893.3 | 100 |
| 24 | A | 3078.9 | 15.4 | 2 |
| 25 | A | 3114.3 | 4.4 | 0 |
| 26 | A | 3135.4 | 5.5 | 1 |
| 27 | A | 3386.2 | 62.5 | 7 |

## TS 39 → 28

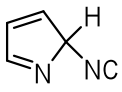


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | 1.32241324 | -1.02228045 | 0.00012625 |
| C | 1.94820458 | 0.24558700 | 0.00003350 |
| C | 0.94264316 | 1.21777016 | -0.00004455 |
| C | -0.25632735 | 0.50344413 | 0.00003123 |
| N | -0.00900058 | -0.91038317 | 0.00013803 |
| H | 1.79273164 | -1.99885885 | 0.00019232 |
| H | 3.01506661 | 0.42660021 | 0.00002858 |
| H | 1.05552032 | 2.29299427 | -0.00012716 |
| H | -1.64523372 | -1.09834547 | -0.00005627 |
| C | -1.63587634 | 0.47740816 | -0.00011502 |
| N | -2.58306065 | -0.25446885 | -0.00017030 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2795645
Zero-point correction= 0.073589 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.205975
Imaginary frequency: -1387.4 $cm^{-1}$

## 40

2-Isocyano-2*H*-pyrrole

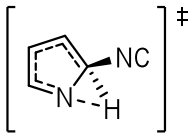


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | 0.34284406 | -0.02942510 | 0.55250234 |
| C | -1.57190214 | -0.73147760 | -0.26767965 |
| C | -1.65169286 | 0.74351408 | -0.28446587 |

| | | | |
|---|---|---|---|
| C | -0.47605445 | 1.19242880 | 0.17828425 |
| H | 0.44386467 | -0.07811824 | 1.64796697 |
| H | -2.37264676 | -1.39687884 | -0.58556474 |
| H | -2.50366679 | 1.32545661 | -0.61587489 |
| H | -0.13805341 | 2.21229338 | 0.31225044 |
| N | -0.45355579 | -1.20623666 | 0.15826479 |
| N | 1.64500858 | -0.04851989 | -0.01219485 |
| C | 2.72852752 | -0.05494969 | -0.47551896 |

State=1-A
RB3LYP/6-31G(d), HF= -302.3419225
Zero-point correction= 0.079934 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.261989

## TS 40 → 41

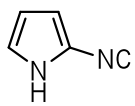



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 0.42190617 | -1.18087337 | -0.01426701 |
| C | -0.36803045 | 0.03851942 | 0.16658957 |
| C | 0.47202736 | 1.17188798 | 0.07229933 |
| C | 1.76187198 | 0.68311395 | -0.10405263 |
| C | 1.68996276 | -0.71842414 | -0.11491659 |
| H | -0.04965309 | -0.77773291 | 1.12003571 |
| H | 0.14467239 | 2.20106907 | 0.12759095 |
| H | 2.66667571 | 1.27385455 | -0.17973260 |
| H | 2.50941838 | -1.42622549 | -0.13867471 |
| C | -2.90553825 | -0.00802813 | -0.14878100 |
| N | -1.73231671 | -0.00103801 | -0.00802604 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2902398
Zero-point correction= 0.075657 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.214583
Imaginary frequency: -1548.7 $cm^{-1}$

## 41

2-Isocyano-1*H*-pyrrole

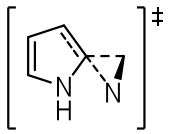



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | 1.72669355 | -0.67929086 | 0.00000000 |

| | | | |
|---|---|---|---|
| C | 1.78465459 | 0.70011620 | 0.00000000 |
| C | 0.45268980 | 1.19021748 | 0.00000000 |
| C | -0.37949291 | 0.08513508 | 0.00000000 |
| N | 0.40588948 | -1.04838679 | 0.00000000 |
| H | 0.04629257 | -1.99105088 | 0.00000000 |
| H | 2.51056670 | -1.42218752 | 0.00000000 |
| H | 2.68778135 | 1.29421314 | 0.00000000 |
| H | 0.12438624 | 2.21936438 | 0.00000000 |
| N | -1.74073921 | -0.00815349 | 0.00000000 |
| C | -2.92205816 | -0.08027076 | 0.00000000 |

State=1-A'
RB3LYP/6-31G(d), HF= -302.3755225
Zero-point correction= 0.080890 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.294632

## TS 41 → 28

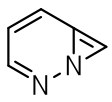


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | 1.64618078 | -0.67675002 | 0.08014007 |
| C | 1.67973193 | 0.70479956 | 0.06271978 |
| C | 0.34857632 | 1.16426256 | -0.09754177 |
| C | -0.45676087 | 0.04035296 | -0.21030802 |
| N | 0.33962196 | -1.07270103 | -0.05952629 |
| H | 2.44122281 | -1.40436991 | 0.15484543 |
| H | 2.56560389 | 1.31649725 | 0.16181616 |
| H | -0.00191176 | 2.18553471 | -0.12651656 |
| C | -1.97319556 | -0.11849968 | -0.52530138 |
| N | -2.12302247 | 0.10694990 | 0.64549514 |
| H | 0.01169302 | -2.02239644 | -0.15017906 |

State=1-A
RB3LYP/6-31G(d), HF= -302.3174114
Zero-point correction= 0.078592 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.238820
Imaginary frequency: -433.5 $cm^{-1}$

## 42

1,2-Diazabicyclo[4.1.0]hepta-2,4,6-triene



Atom Coordinates (Angstroms)

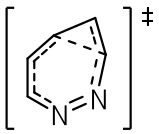
| Type | X | Y | Z |
|---|---|---|---|
| N | -0.19095993 | -1.43233188 | -0.06840100 |
| C | -0.63781238 | 0.95695541 | -0.03692800 |
| C | -1.69143275 | 0.38219510 | 0.42630200 |
| C | 0.72938989 | 1.36507253 | -0.09074300 |
| C | 1.56265720 | 0.30416499 | 0.04111500 |
| C | 1.00833932 | -1.04254065 | 0.22723200 |
| H | -2.50427383 | 0.26013763 | 1.12497700 |
| H | 1.05182155 | 2.39364232 | -0.21766100 |
| H | 2.64177428 | 0.42402828 | 0.03794300 |
| H | 1.67756582 | -1.82233809 | 0.59035000 |
| N | -1.05100328 | -0.43203232 | -0.63695400 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2406907
Zero-point correction= 0.077462 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.163229

**Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):**

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A | 148.3 | 4.5 | 8 |
| 2 | A | 304.3 | 16.5 | 28 |
| 3 | A | 356.6 | 8.9 | 15 |
| 4 | A | 419.7 | 1.1 | 2 |
| 5 | A | 549.0 | 11.0 | 19 |
| 6 | A | 564.2 | 1.4 | 2 |
| 7 | A | 603.8 | 9.1 | 15 |
| 8 | A | 654.5 | 9.1 | 15 |
| 9 | A | 713.2 | 59.4 | 101 |
| 10 | A | 767.0 | 6.1 | 10 |
| 11 | A | 850.3 | 1.8 | 3 |
| 12 | A | 905.7 | 4.2 | 7 |
| 13 | A | 926.3 | 3.9 | 7 |
| 14 | A | 947.6 | 7.4 | 12 |
| 15 | A | 950.8 | 2.7 | 5 |
| 16 | A | 982.2 | 1.3 | 2 |
| 17 | A | 1010.2 | 8.6 | 15 |
| 18 | A | 1119.6 | 3.7 | 6 |
| 19 | A | 1307.5 | 3.3 | 6 |
| 20 | A | 1346.4 | 8.1 | 14 |
| 21 | A | 1480.2 | 5.7 | 10 |
| 22 | A | 1573.9 | 4.1 | 7 |
| 23 | A | 1829.8 | 10.5 | 18 |
| 24 | A | 3033.4 | 19.7 | 33 |
| 25 | A | 3077.7 | 1.4 | 2 |
| 26 | A | 3094.8 | 7.9 | 13 |
| 27 | A | 3183.9 | 6.6 | 11 |

## TS 42 → 43

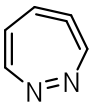


| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -0.22610231 | -1.42444011 | -0.09663400 |
| C | -0.61299349 | 1.00300270 | -0.02250800 |
| C | -1.65491420 | 0.41040319 | 0.43791800 |
| C | 0.76398334 | 1.35032537 | -0.11169000 |
| C | 1.56220487 | 0.26624976 | 0.05995500 |
| C | 0.97415552 | -1.06185952 | 0.23939600 |
| H | -2.45541114 | 0.29523780 | 1.15319800 |
| H | 1.12211885 | 2.35722055 | -0.30142600 |
| H | 2.64454383 | 0.35123929 | 0.04224700 |
| H | 1.62113091 | -1.86597621 | 0.58807000 |
| N | -1.07775479 | -0.42505353 | -0.63201100 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2406546
Zero-point correction= 0.077046 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.163609
Imaginary frequency: -182.5 $cm^{-1}$

## 43

1,2-Diazacyclohepta-1,3,4,6-tetraene



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -1.41396631 | 0.02941632 | -0.27724003 |
| C | 1.18229604 | -0.74247263 | 0.08016611 |
| N | -1.04167157 | -1.15459167 | -0.43845544 |
| C | -0.79412338 | 1.11766828 | 0.31664271 |
| C | 0.53303844 | 1.48498559 | 0.19491349 |
| H | 0.79977355 | 2.53118672 | 0.34892864 |
| H | -1.52497691 | 1.84973297 | 0.64886425 |
| C | 0.17024199 | -1.53294958 | 0.32540476 |
| H | 0.08409034 | -2.40668799 | 0.95997794 |
| C | 1.48898870 | 0.52348152 | -0.26327629 |
| H | 2.34792737 | 0.79771663 | -0.87100720 |

State=1-A
RB3LYP/6-31G(d), HF= -302.2755361
Zero-point correction= 0.078875 (Hartree/Particle)
Sum of electronic and zero-point Energies= -302.196661

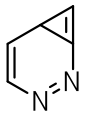
**Vibrational Frequencies (B3LYP/6-311G**, scaled by 0.967):**

| ModeNr. | Symmetry | Wavenumber | Abs.Int. | Rel.Int. |
|---|---|---|---|---|
| 1 | A | 263.4 | 21.8 | 26 |
| 2 | A | 328.0 | 2.9 | 3 |
| 3 | A | 350.1 | 9.1 | 11 |
| 4 | A | 435.3 | 5.5 | 6 |
| 5 | A | 515.9 | 15.9 | 19 |
| 6 | A | 602.8 | 22.5 | 27 |
| 7 | A | 663.1 | 9.6 | 11 |
| 8 | A | 701.6 | 48.0 | 57 |
| 9 | A | 753.7 | 31.3 | 37 |
| 10 | A | 807.8 | 27.5 | 32 |
| 11 | A | 822.1 | 8.4 | 10 |
| 12 | A | 848.6 | 50.4 | 59 |
| 13 | A | 915.4 | 2.7 | 3 |
| 14 | A | 937.2 | 3.7 | 4 |
| 15 | A | 1019.2 | 7.5 | 9 |
| 16 | A | 1083.4 | 2.3 | 3 |
| 17 | A | 1173.5 | 19.3 | 23 |
| 18 | A | 1202.9 | 8.2 | 10 |
| 19 | A | 1314.1 | 8.3 | 10 |
| 20 | A | 1399.5 | 9.1 | 11 |
| 21 | A | 1453.5 | 12.0 | 14 |
| 22 | A | 1511.8 | 84.9 | 100 |
| 23 | A | 1816.8 | 3.4 | 4 |
| 24 | A | 3027.0 | 20.1 | 24 |
| 25 | A | 3061.4 | 9.3 | 11 |
| 26 | A | 3078.0 | 8.2 | 10 |
| 27 | A | 3117.2 | 1.9 | 2 |

**Table S3. Cartesian coordinates and CASPT2 energies of species optimized at CASSCF(8,8)/6-31G* level using MOLCAS.**

## 16

2,3-Diazabicyclo[4.1.0]hepta-1(7),2,4-triene



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -1.4774752 | -0.5956947 | 0.0575605 |
| N | -0.5503553 | -1.4172458 | -0.1744105 |
| C | 0.7140623 | -0.8320816 | -0.1931738 |
| C | 1.6703515 | -0.3216284 | 0.5270965 |
| C | 1.0806772 | 0.6185427 | -0.4857561 |
| C | -0.0725271 | 1.4388329 | -0.0579099 |
| C | -1.2196294 | 0.7855045 | 0.2521470 |
| H | 2.1351355 | -0.3206816 | 1.4890472 |
| H | 1.6310305 | 0.8994088 | -1.3688660 |
| H | -0.0436028 | 2.5141940 | -0.0328571 |
| H | -2.0972033 | 1.3101600 | 0.5756541 |

QCISD(T)/6-31G* on CAS(8,8)/6-31G* geometry: -301.4023458

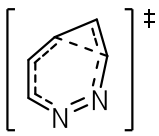
CASSCF Reference energy: -300.4833719120
CASPT2 Total energy: -301.3185401325
Residual norm: 0.0000009957
Reference weight: 0.78371

CAS(8,8) active space: 3 π/π* pairs and σ/σ* of C3-C4 bond.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | 0.921242 | 0.848686 |

## TS 16 → 17



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 1.5707959 | -0.2620997 | 0.0469429 |
| N | 0.8428989 | -1.2639291 | -0.3361654 |

| | | | |
|---|---|---|---|
| C | -0.4578175 | -1.0816196 | -0.1427027 |
| C | -1.4655664 | -0.6533612 | 0.5499319 |
| C | -1.2806560 | 0.4858345 | -0.3726214 |
| C | -0.2337963 | 1.4014256 | -0.0804897 |
| C | 1.0347391 | 0.9623780 | 0.2871384 |
| H | -1.9393050 | -0.8132502 | 1.4952505 |
| H | -1.9688222 | 0.6737495 | -1.1798046 |
| H | -0.3510678 | 2.4484764 | -0.3039616 |
| H | 1.7780942 | 1.6851917 | 0.5652350 |

QCISD(T)/6-31G* on CAS(8,8)/6-31G* geometry: -301.4003518
Barrier is about 1.3 kcal/mol cf. **16**.

CASSCF Reference energy: -300.4724881615
CASPT2 Total energy: -301.3190247140
Residual norm: 0.0000003753
Reference weight: 0.77972

CAS(8,8) active space: 3 $\pi/\pi^*$ pairs and $\sigma/\sigma^*$ of breaking C3-C4 bond.

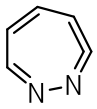
Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | -0.914106 | 0.835590 |

Imaginary frequency: -756.8 $cm^{-1}$

## 17

1,2-Diazacyclohepta-2,3,5,7-tetraene




| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 1.6188383 | 0.0364796 | 0.2121174 |
| N | 1.0478870 | -1.0297447 | -0.5068398 |
| C | -0.0637449 | -1.3717369 | -0.0326381 |
| C | -1.2607627 | -0.9229212 | 0.3455433 |
| C | -1.5288088 | 0.4421654 | -0.1318956 |
| C | -0.5054320 | 1.3273020 | -0.2177470 |
| C | 0.8819195 | 1.0915178 | 0.2526488 |
| H | -1.9311988 | -1.4650136 | 0.9822202 |
| H | -2.5286283 | 0.7458257 | -0.3895322 |
| H | -0.7091336 | 2.3347691 | -0.5358253 |
| H | 1.3628571 | 1.9393120 | 0.7107251 |

CASSCF Reference energy: -300.5335373130
CASPT2 Total energy: -301.3587833819
Residual norm: 0.0000003930
Reference weight: 0.78585

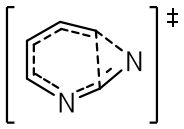
CAS(8,8) active space: 4 π/π* pairs

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | -0.905147 | 0.819292 |

## TS 17 → 19

*NB:* the diazirine structure **18** is a TS at the CAS(8,8)/6-31G* level, but an intermediate at the B3LYP/6-31G* level.



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 1.3335107 | 0.3471569 | -0.4375815 |
| N | 1.3001472 | -0.6950332 | 0.6022249 |
| C | 0.3838722 | -1.1190318 | -0.1181254 |
| C | 0.4400056 | 1.3380621 | -0.1377111 |
| C | -0.8719521 | 1.1908390 | 0.2769910 |
| C | -1.6151648 | -0.0117026 | 0.0939952 |
| C | -1.0041814 | -1.1949430 | -0.2628298 |
| H | 0.7896907 | 2.3128707 | -0.4284905 |
| H | -1.4214230 | 2.0892659 | 0.4898067 |
| H | -2.6886436 | 0.0485591 | 0.1074659 |
| H | -1.5035724 | -2.0370420 | -0.6960463 |

CASSCF Reference energy: -300.4901589243
CASPT2 Total energy: -301.3356436933
Residual norm: 0.0000004153
Reference weight: 0.77877

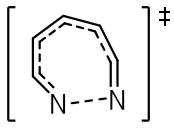
CAS(8,8) active space: 4 π/π* pairs.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | -0.910367 | 0.828768 |

Imaginary frequency: -745.0 $cm^{-1}$

## TS 17 → 23ZZ $S_1$



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|

| | | | |
|---|---|---|---|
| N | 1.1201475 | -1.2340061 | -0.5986258 |
| N | 1.7140631 | 0.4255292 | 0.2830841 |
| C | 0.7583148 | 1.2679604 | 0.2017204 |
| C | -0.6642102 | 1.2618903 | -0.2331447 |
| C | -1.5686139 | 0.2951191 | -0.0723658 |
| C | -1.1728067 | -1.0375190 | 0.3778306 |
| C | 0.0609987 | -1.4005549 | -0.0465723 |
| H | 1.0513019 | 2.2332118 | 0.5981788 |
| H | -1.0051258 | 2.2311399 | -0.5509465 |
| H | -2.6094161 | 0.5044832 | -0.2501523 |
| H | -1.7597554 | -1.6280653 | 1.0518256 |

CASSCF Reference energy: -300.5266957437
CASPT2 Total energy: -301.3372687687
Residual norm: 0.0000006643
Reference weight: 0.78136

CAS(8,8) active space: 3 $\pi/\pi^*$ pairs and $\sigma/\sigma^*$ of N1-N2 bond.

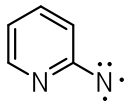
Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | 0.868007 | 0.753436 |

Imaginary frequency: -446.9 $cm^{-1}$

## 19 $T_0$

2-Pyridyl-nitrene



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -0.3911211 | -1.2133697 | 0.0000000 |
| N | -2.3631868 | -0.0195974 | 0.0000000 |
| C | 1.0782569 | 1.1857283 | 0.0000000 |
| C | -0.3109027 | 1.2183804 | 0.0000000 |
| C | -1.0146108 | -0.0096933 | 0.0000000 |
| C | 0.9273629 | -1.2203849 | 0.0000000 |
| C | 1.7169063 | -0.0549133 | 0.0000000 |
| H | 1.6464144 | 2.0976726 | 0.0000000 |
| H | -0.8584402 | 2.1417152 | 0.0000000 |
| H | 1.3953693 | -2.1885509 | 0.0000000 |
| H | 2.7877755 | -0.1326867 | 0.0000000 |

CASSCF Reference energy: -300.5894702442
CASPT2 Total energy: -301.3993493799
Residual norm: 0.0000002835
Reference weight: 0.79153

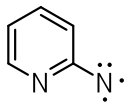
CAS(8,8) active space: 3 $\pi/\pi^*$ pairs and $p_y/p_z$ AO on nitrene N.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation(a',a") | Coef | Weight |
|---|---|---|---|
| 1 | u,222u000 | 0.912759 | 0.833129 |

## 19 $S_1$

2-Pyridyl-nitrene



| Atom Type | X | Y | Z |
|---|---|---|---|
| N | 0.0159740 | 2.3293780 | 0.0000000 |
| N | -1.2503770 | 0.4033240 | 0.0000000 |
| C | 0.0000000 | 1.0541670 | 0.0000000 |
| C | 1.2537260 | 0.2826480 | 0.0000000 |
| C | 1.1946790 | -1.0863770 | 0.0000000 |
| C | -0.0710020 | -1.7154340 | 0.0000000 |
| C | -1.2520740 | -0.8893970 | 0.0000000 |
| H | 2.1811400 | 0.8213670 | 0.0000000 |
| H | 2.0936010 | -1.6747220 | 0.0000000 |
| H | -0.1683650 | -2.7834420 | 0.0000000 |
| H | -2.2175250 | -1.3657620 | 0.0000000 |

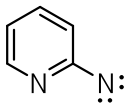
CASSCF Reference energy: -300.5598854554
CASPT2 Total energy: -301.3679226446
Residual norm: 0.0000005313
Reference weight: 0.79137

CAS(8,8) active space: 3 π/π* pairs and $p_y/p_z$ AO on nitrene N.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation(a',a") | Coef | Weight |
|---|---|---|---|
| 1 | u,222d000 | 0.916812 | 0.840544 |

## 19 $S_2$



| Atom Type | X | Y | Z |
|---|---|---|---|
| N | -1.1986333 | 0.4059067 | 0.0000000 |
| N | 0.0337078 | 2.3828314 | 0.0000000 |
| C | 0.0053437 | 1.0073353 | 0.0000000 |
| C | 1.2113761 | 0.2940834 | 0.0000000 |
| C | 1.1670565 | -1.1008939 | 0.0000000 |
| C | -0.0775243 | -1.7181387 | 0.0000000 |
| C | -1.2289406 | -0.9165973 | 0.0000000 |

| | | | |
|---|---|---|---|
| H | 2.1402237 | 0.8316956 | 0.0000000 |
| H | 2.0727412 | -1.6790783 | 0.0000000 |
| H | -0.1698087 | -2.7883372 | 0.0000000 |
| H | -2.2042740 | -1.3692470 | 0.0000000 |

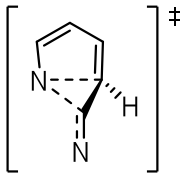
CASSCF Reference energy: -300.5204367231
CASPT2 Total energy: -301.3394930540
Residual norm: 0.0000005443
Reference weight: 0.78868

CAS(8,8) active space: 3 π/π* pairs and $p_y/p_z$ AO on nitrene N.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation(a',a") | Coef | Weight |
|---|---|---|---|
| 1 | 2,2220000 | -0.764339 | 0.584215 |

## TS 19 → 33




| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -0.2980473 | -0.8987863 | 0.6911575 |
| N | -2.2469765 | -0.0356512 | -0.5978746 |
| C | 0.9107505 | -1.1657473 | 0.0251580 |
| C | 1.6619958 | -0.1141638 | -0.3947572 |
| C | 1.0573725 | 1.1389593 | -0.0716124 |
| C | -0.2454032 | 1.0606559 | 0.4016722 |
| C | -1.1488825 | -0.0636510 | -0.0484851 |
| H | 1.1279586 | -2.2065639 | -0.1193616 |
| H | 2.6031764 | -0.2193324 | -0.8970963 |
| H | 1.5823803 | 2.0745693 | -0.0950136 |
| H | -0.7004442 | 1.7837038 | 1.0494853 |

CASSCF Reference energy: -300.4815749901
CASPT2 Total energy: -301.3240028692
Residual norm: 0.0000001958
Reference weight: 0.77633

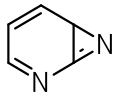
CAS(8,8) active space: 3 π/π* pairs and σ/σ* of new N1-C3 bond.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | 0.816899 | 0.667324 |
| 18 | 22202000 | -0.397123 | 0.157707 |

Imaginary frequency: -694.1 $cm^{-1}$

## 20



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -1.6317404 | -0.4328864 | 0.6902082 |
| N | 0.4532494 | -1.4431738 | -0.1931727 |
| C | 1.2462433 | 0.8520171 | 0.1927153 |
| C | 0.0662103 | 1.4752390 | -0.0629313 |
| C | 1.4162130 | -0.6032416 | -0.0099117 |
| C | -0.7431970 | -0.7477093 | -0.1346967 |
| C | -1.0571379 | 0.6077189 | -0.4616054 |
| H | 2.4176613 | -0.9972894 | -0.0236403 |
| H | 2.1216862 | 1.4117466 | 0.4667107 |
| H | -0.0159476 | 2.5470708 | -0.0346315 |
| H | -1.7697314 | 0.8915892 | -1.2103377 |

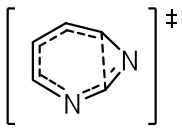
CASSCF Reference energy: -300.5606827649
CASPT2 Total energy: -301.3832684644
Residual norm: 0.0000009972
Reference weight: 0.78799

CAS(8,8) active space: 3 π/π* pairs and σ/σ* of azirene C3-N bond.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | -0.922280 | 0.850600 |

## TS 20 → 21



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -1.4663864 | -0.5049669 | 0.6193171 |
| N | 0.6081082 | -1.3933502 | -0.3641567 |
| C | 1.1427358 | 0.8879992 | 0.2841518 |
| C | -0.0966195 | 1.4293716 | -0.0983394 |
| C | -0.5988059 | -0.9600375 | -0.1456898 |
| C | -1.2207758 | 0.6242695 | -0.3173877 |
| C | 1.4753570 | -0.4565878 | 0.0455306 |
| H | 1.9514619 | 1.5583657 | 0.5097608 |
| H | -0.1295885 | 2.4603233 | -0.4066188 |
| H | 2.5074176 | -0.7541538 | 0.0629645 |
| H | -2.0183053 | 0.8886026 | -0.9844003 |

CASSCF Reference energy: -300.5300561875

CASPT2 Total energy: -301.3804825475
Residual norm: 0.0000005280
Reference weight: 0.77952

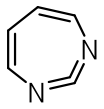
CAS(8,8) active space: 3 π/π* pairs and σ/σ* of breaking C-C bond.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | 0.925826 | 0.857153 |

Imaginary frequency: -891.0 $cm^{-1}$

## 21



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 1.1337848 | -1.0410897 | 0.4442020 |
| N | -1.1336342 | -1.0408875 | -0.4441576 |
| C | 0.0000489 | -1.2797882 | -0.0000237 |
| C | 1.5642903 | 0.2045207 | -0.1186450 |
| C | 0.7132113 | 1.2506975 | -0.1986706 |
| C | -0.7132966 | 1.2508039 | 0.1986944 |
| C | -1.5643419 | 0.2046095 | 0.1186602 |
| H | 2.5962859 | 0.2686199 | -0.4027736 |
| H | 1.1122206 | 2.1906219 | -0.5360996 |
| H | -1.1121945 | 2.1907840 | 0.5360910 |
| H | -2.5963565 | 0.2685198 | 0.4027445 |

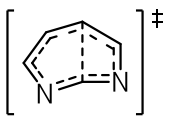
CASSCF Reference energy: -300.5680080915
CASPT2 Total energy: -301.3986077829
Residual norm: 0.0000008171
Reference weight: 0.78576

CAS(8,8) active space: 4 π/π* pairs.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | 0.923982 | 0.853743 |

## TS 21 → 24



Atom Coordinates (Angstroms)

| Type | X | Y | Z |
|---|---|---|---|
| N | 1.3562079 | -0.9099496 | -0.3345003 |
| N | -1.0437026 | -1.2100536 | 0.1941827 |
| C | -1.6556620 | 0.0307613 | -0.2073834 |
| C | -0.8814688 | 1.1423984 | -0.2278035 |
| C | 0.4792400 | 1.0870605 | 0.3878995 |
| C | 0.1634543 | -0.8830860 | 0.2554813 |
| C | 1.6276237 | 0.3727598 | -0.0975306 |
| H | -2.6635492 | -0.0411703 | -0.5642994 |
| H | -1.2880686 | 2.0825642 | -0.5559419 |
| H | 0.6654700 | 1.8845151 | 1.0952827 |
| H | 2.6252504 | 0.7626690 | -0.2234139 |

CASSCF Reference energy: -300.4772578996
CASPT2 Total energy: -301.3249304819
Residual norm: 0.0000004420
Reference weight: 0.77906

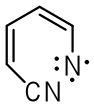
CAS(8,8) active space: 3 π/π* pairs and σ/σ* of new C-C bond.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | -0.914876 | 0.836998 |

Imaginary frequency: -1102.2 $cm^{-1}$

## 23ZZ $T_0$




| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -2.0003763 | -1.5340114 | 0.0000000 |
| N | 1.1910971 | -1.4539090 | 0.0000000 |
| C | -1.5900501 | -0.4618090 | 0.0000000 |
| C | -1.2195257 | 0.9181275 | 0.0000000 |
| C | 0.0297335 | 1.4988204 | 0.0000000 |
| C | 1.3527061 | 0.9863635 | 0.0000000 |
| C | 1.8618694 | -0.3572208 | 0.0000000 |
| H | -2.0656285 | 1.5798105 | 0.0000000 |
| H | -0.0057935 | 2.5740994 | 0.0000000 |
| H | 2.1179670 | 1.7406552 | 0.0000000 |
| H | 2.9383669 | -0.4578584 | 0.0000000 |

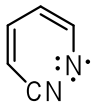
CASSCF Reference energy: -300.5543213940
CASPT2 Total energy: -301.3617603798
Residual norm: 0.0000002000
Reference weight: 0.78517

CAS(8,8) active space: 3 π/π* pairs and $p_y/p_z$ AO on nitrene N.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation(a',a") | Coef | Weight |
|---|---|---|---|
| 1 | u,222u000 | -0.906936 | 0.822534 |

## 23ZZ $S_1$



| Atom Type | X | Y | Z |
|---|---|---|---|
| N | 2.4297152 | 0.6700746 | 0.0000000 |
| N | 0.4445166 | -1.8321483 | 0.0000000 |
| C | 1.3253704 | 0.9925077 | 0.0000000 |
| C | 0.0110854 | 1.5260187 | 0.0000000 |
| C | -1.2392001 | 0.8629464 | 0.0000000 |
| C | -1.6122772 | -0.4629403 | 0.0000000 |
| C | -0.8146170 | -1.7100983 | 0.0000000 |
| H | -0.0135176 | 2.5992993 | 0.0000000 |
| H | -2.0674169 | 1.5496332 | 0.0000000 |
| H | -2.6719916 | -0.6408996 | 0.0000000 |
| H | -1.3878436 | -2.6285554 | 0.0000000 |

CASSCF Reference energy: -300.5426420944
CASPT2 Total energy: -301.3502394249
Residual norm: 0.0000003369
Reference weight: 0.78481

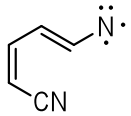
CAS(8,8) active space: 3 π/π* pairs and $p_y/p_z$ AO on nitrene N.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation(a',a") | Coef | Weight |
|---|---|---|---|
| 1 | u,222d000 | 0.921199 | 0.848607 |

## 23EZ $T_0$

*(2E,3s-Z,4Z)*-5-cyanopenta-2,4-dienenitrene



| Atom Type | X | Y | Z |
|---|---|---|---|
| N | -2.0311679 | -1.5858878 | 0.0000000 |
| N | 2.6620615 | -0.9381053 | 0.0000000 |
| C | 1.4347188 | -0.5452268 | 0.0000000 |
| C | 1.1179194 | 0.8547504 | 0.0000000 |
| C | -0.1580975 | 1.4678449 | 0.0000000 |
| C | -1.4233226 | 0.9189266 | 0.0000000 |
| C | -1.7434417 | -0.4739822 | 0.0000000 |

| | | | |
|---|---|---|---|
| H | 0.6679662 | -1.3011312 | 0.0000000 |
| H | 1.9631236 | 1.5181211 | 0.0000000 |
| H | -0.1410006 | 2.5429806 | 0.0000000 |
| H | -2.2730027 | 1.5741031 | 0.0000000 |

CASSCF Reference energy: -300.5635446353
CASPT2 Total energy: -301.3704686023
Residual norm: 0.0000001644
Reference weight: 0.78572

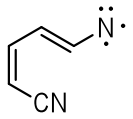
CAS(8,8) active space: 3 π/π* pairs and $p_y/p_z$ AO on nitrene N.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation(a',a") | Coef | Weight |
|---|---|---|---|
| 1 | u,222u000 | 0.906771 | 0.822233 |

## 23EZ $S_1$

*(2E,3s-Z,4Z)*-5-cyanopenta-2,4-dienenitrene




| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -2.0474478 | -1.5748253 | 0.0000000 |
| N | 2.6394639 | -0.9659370 | 0.0000000 |
| C | 1.4354424 | -0.5669430 | 0.0000000 |
| C | 1.1185441 | 0.8758745 | 0.0000000 |
| C | -0.1184613 | 1.4771950 | 0.0000000 |
| C | -1.4204355 | 0.9171994 | 0.0000000 |
| C | -1.7491324 | -0.4633415 | 0.0000000 |
| H | 0.6562148 | -1.3112687 | 0.0000000 |
| H | 1.9766633 | 1.5218116 | 0.0000000 |
| H | -0.1110225 | 2.5524078 | 0.0000000 |
| H | -2.2617127 | 1.5824794 | 0.0000000 |

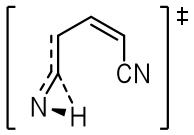
CASSCF Reference energy: -300.5519125942
CASPT2 Total energy: -301.3589529872
Residual norm: 0.0000002915
Reference weight: 0.78539

CAS(8,8) active space: 3 π/π* pairs and $p_y/p_z$ AO on nitrene N.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation(a',a") | Coef | Weight |
|---|---|---|---|
| 1 | u,222d000 | 0.922211 | 0.850472 |

## TS 23EZ → 26Z

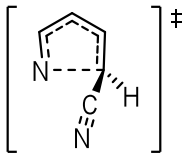



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| C | -1.526704 | -0.181267 | 0.033780 |
| C | -1.071115 | 1.122366 | 0.105947 |
| C | 0.302864 | 1.546349 | -0.031876 |
| C | 1.441299 | 0.818970 | -0.128777 |
| C | 1.498302 | -0.612774 | -0.003758 |
| N | 1.549223 | -1.752134 | 0.122845 |
| N | -2.042176 | -1.262538 | -0.258732 |
| H | -1.430992 | -0.833769 | 0.991271 |
| H | -1.793630 | 1.845968 | 0.432299 |
| H | 0.423475 | 2.614607 | -0.067189 |
| H | 2.383949 | 1.314036 | -0.257062 |

CASSCF Reference energy: -300.5024792039
CASPT2 Total energy: -301.3318089537
Residual norm: 0.0000009430
Reference weight: 0.77641

CAS(8,8) active space: 3 π/π* pairs and σ/σ* of breaking C-H bond.

## TS 23ZZ → 32




| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -2.3963287 | -0.5470579 | -0.4871501 |
| N | 0.6654827 | -1.5552010 | 0.7789819 |
| C | 1.3974378 | -1.0749930 | -0.1361468 |
| C | 1.5585379 | 0.3741556 | -0.3985922 |
| C | 0.6538019 | 1.3258248 | -0.0791418 |
| C | -0.6900093 | 1.1249088 | 0.4493236 |
| C | -1.6135959 | 0.1816822 | -0.0604113 |
| H | 1.9568327 | -1.7679546 | -0.7495956 |
| H | 2.4925455 | 0.6729588 | -0.8388394 |
| H | 0.9445795 | 2.3548614 | -0.2022840 |
| H | -1.1013937 | 1.8716337 | 1.1012245 |

CASSCF Reference energy: -300.5425141214
CASPT2 Total energy: -301.3509238749
Residual norm: 0.0000003821
Reference weight: 0.78440

CAS(8,8) active space: 3 π/π* pairs and σ/σ* of new N1-C3 bond.

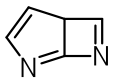
Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | 0.722921 | 0.522615 |
| 18 | 22202000 | -0.580152 | 0.336577 |

Imaginary frequency: -195.0 $cm^{-1}$

## 24

2,7-diazabicyclo[3.2.0]hepta-1,3,6-triene



| Atom Type | X | Y | Z |
|---|---|---|---|
| N | -1.6426273 | -0.7608699 | -0.1230026 |
| N | 0.8065958 | -1.2198895 | -0.0346273 |
| C | -0.2571680 | -0.6631235 | 0.4141463 |
| C | -1.5619806 | 0.5135369 | -0.3168329 |
| C | -0.2618112 | 0.8414124 | 0.4309665 |
| C | 1.1045808 | 1.0828678 | -0.1360534 |
| C | 1.7007143 | -0.1348507 | -0.2290637 |
| H | -2.2776144 | 1.1168959 | -0.8447048 |
| H | -0.4511322 | 1.3527583 | 1.3668202 |
| H | 1.6007476 | 2.0297425 | -0.2179627 |
| H | 2.7176539 | -0.3443378 | -0.4949226 |

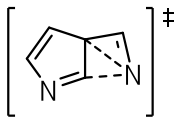
CASSCF Reference energy: -300.5496100247
CASPT2 Total energy: -301.3790610879
Residual norm: 0.0000002666
Reference weight: 0.78529

CAS(8,8) active space: 3 π/π* pairs and σ/σ* of C1-N7 bond.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | 0.923540 | 0.852927 |

## TS 24 → 25



| Atom Type | X | Y | Z |
|---|---|---|---|
| N | -1.8686721 | 0.6562185 | 0.3790679 |
| N | 0.5837618 | -1.2681430 | -0.0286577 |

| | | | |
|---|---|---|---|
| C | 1.6555112 | -0.4637151 | 0.3773532 |
| C | 1.3871002 | 0.8809789 | 0.3015801 |
| C | 0.1051104 | 0.9792871 | -0.3271864 |
| C | -0.2901917 | -0.4370165 | -0.5068148 |
| C | -1.7323700 | -0.4319351 | -0.2682639 |
| H | 2.5665895 | -0.9290483 | 0.6975009 |
| H | 2.0627326 | 1.6812735 | 0.5244902 |
| H | -0.2212564 | 1.7936492 | -0.9391058 |
| H | -2.4932652 | -1.1731723 | -0.4287397 |

CASSCF Reference energy: -300.5342278096
CASPT2 Total energy: -301.3629647078
Residual norm: 0.0000007053
Reference weight: 0.78366

CAS(8,8) active space: 3 π/π* pairs and σ/σ* of breaking C1-N7 bond.

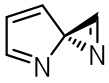
Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | -0.883835 | 0.781164 |

Imaginary frequency: -334.1 $cm^{-1}$

## 25

1,4-diazaspiro[2.4]hepta-1,4,6-triene



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 1.7876386 | -0.0326960 | -0.6980371 |
| N | -0.3287413 | -1.1812136 | 0.0144410 |
| C | -1.5607773 | -0.7563679 | 0.0102738 |
| C | -1.6708891 | 0.7162495 | 0.0093480 |
| C | -0.4101857 | 1.1859059 | 0.0146566 |
| C | 0.4846195 | 0.0001991 | 0.0437464 |
| C | 1.8307237 | -0.0517817 | 0.5491341 |
| H | -2.3871624 | -1.4426732 | 0.0006775 |
| H | -2.5863966 | 1.2734417 | -0.0066241 |
| H | -0.0728262 | 2.2031739 | 0.0049076 |
| H | 2.5297313 | -0.1065505 | 1.3581546 |

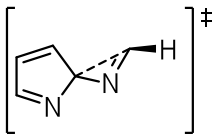
CASSCF Reference energy: -300.5751012351
CASPT2 Total energy: -301.3979184163
Residual norm: 0.0000004157
Reference weight: 0.78681

CAS(8,8) active space: 3 π/π* pairs and σ/σ* of azirene C-N bond.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | -0.934688 | 0.873641 |

## TS 25 → 36



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 1.7329828 | -0.2771058 | -0.3796518 |
| N | -0.4838502 | -1.1072127 | 0.1016688 |
| C | 0.3246746 | -0.0901963 | -0.1783008 |
| C | 2.2190421 | 0.1287332 | 0.6979649 |
| C | -0.3851399 | 1.1853543 | -0.2565322 |
| C | -1.6867841 | 0.8725104 | -0.0327525 |
| C | -1.7046778 | -0.5682898 | 0.1866702 |
| H | 3.2373444 | 0.1177232 | 1.0519435 |
| H | 0.0593586 | 2.1345242 | -0.4745170 |
| H | -2.5360671 | 1.5248826 | -0.0194601 |
| H | -2.5647956 | -1.1790186 | 0.3768440 |

CASSCF Reference energy: -300.5073971641
CASPT2 Total energy: -301.3324021477
Residual norm: 0.0000007407
Reference weight: 0.78667

CAS(8,8) active space: 3 π/π* pairs and σ/σ* of new C-C bond.

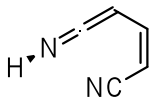
Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | 0.766089 | 0.586893 |
| 18 | 22202000 | -0.523796 | 0.274362 |

Imaginary frequency: -513.4 $cm^{-1}$

## 26Z

*(s-Z,Z)*-5-Iminopenta-2,4-dienenitrile



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -1.4341479 | -1.7740077 | 0.3497841 |
| N | 2.0733510 | -0.9948844 | -0.4184475 |
| C | 1.5200149 | 0.0171684 | 0.0037830 |
| C | 0.9758636 | 1.1946989 | 0.2674259 |
| C | -0.3980873 | 1.5629704 | -0.1001113 |
| C | -1.4587315 | 0.7704805 | -0.1996797 |

| | | | |
|---|---|---|---|
| C | -1.4368207 | -0.6414179 | 0.0987330 |
| H | 1.9859208 | -1.7930066 | 0.1904218 |
| H | 1.5774211 | 1.9233621 | 0.7788094 |
| H | -0.5497607 | 2.6090814 | -0.3016018 |
| H | -2.4083465 | 1.1679530 | -0.5029171 |

CASSCF Reference energy: -300.6183914724
CASPT2 Total energy: -301.4154924170
Residual norm: 0.0000006404
Reference weight: 0.79055

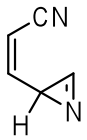
CAS(8,8) active space: 4 π/π* pairs.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | 0.938094 | 0.880021 |

## 30

*(Z)*-3-(2*H*-azirin-2-yl)acrylonitrile




| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 1.8502010 | -0.7490662 | -0.7378573 |
| N | -2.2729115 | -0.9310095 | 0.2748188 |
| C | 1.1108572 | -1.1446390 | 0.1885307 |
| C | 1.3460426 | 0.2597479 | 0.3957461 |
| C | 0.4090173 | 1.3353271 | -0.0139031 |
| C | -0.9015977 | 1.2374857 | -0.1760680 |
| C | -1.6532992 | 0.0274148 | 0.0684535 |
| H | 0.6300876 | -2.0440412 | 0.5154779 |
| H | 2.1300024 | 0.5721925 | 1.0636446 |
| H | 0.8591725 | 2.2965107 | -0.1946916 |
| H | -1.4802511 | 2.0827472 | -0.4977987 |

CASSCF Reference energy: -300.6014492548
CASPT2 Total energy: -301.3906441724
Residual norm: 0.0000008426
Reference weight: 0.79308

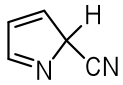
CAS(8,8) active space: 3 π/π* pairs and σ/σ* of azirene C-N bond.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | -0.938649 | 0.881062 |

## 32

2*H*-Pyrrole-2-carbonitrile



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 0.4704004 | -1.1915459 | 0.2289863 |
| N | -2.6902971 | -0.0037407 | -0.4993287 |
| C | -1.6378858 | -0.0300169 | -0.0174490 |
| C | -0.3011022 | -0.0097836 | 0.6116563 |
| C | 0.5358596 | 1.1828863 | 0.2010087 |
| C | 1.6767400 | 0.7045707 | -0.3195484 |
| C | 1.5714004 | -0.7685673 | -0.2727381 |
| H | -0.4408210 | -0.0385998 | 1.6873075 |
| H | 0.2356471 | 2.2029059 | 0.3339779 |
| H | 2.5120070 | 1.2588312 | -0.6991078 |
| H | 2.3240207 | -1.4547923 | -0.6156037 |

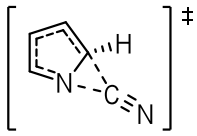
CASSCF Reference energy: -300.6578065280
CASPT2 Total energy: -301.4509614480
Residual norm: 0.0000008676
Reference weight: 0.79758

CAS(8,8) active space: 4 π/π* pairs.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | -0.925462 | 0.856480 |

## TS 32 → 33



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -0.1263340 | -0.5613110 | 0.8182420 |
| N | -2.2827450 | -0.0438950 | -0.6618010 |
| C | 0.8630660 | -1.1453530 | 0.0854470 |
| C | 1.6726850 | -0.1868650 | -0.5212930 |
| C | 1.1501620 | 1.0692160 | -0.2195060 |
| C | 0.0125270 | 0.8461710 | 0.5920850 |
| C | -1.2666140 | 0.0436040 | -0.0861640 |
| H | 0.8775220 | -2.2082390 | -0.0356870 |
| H | 2.5263240 | -0.3907940 | -1.1363080 |
| H | 1.5123040 | 2.0243790 | -0.5388960 |
| H | -0.3989150 | 1.5207340 | 1.3164890 |

CASSCF Reference energy: -300.5417046639
CASPT2 Total energy: -301.3829899982

Residual norm: 0.0000007328
Reference weight: 0.78180

CAS(8,8) active space: 4 π/π* pairs.

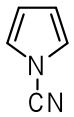
Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | 0.925803 | 0.857112 |

Imaginary frequency: -1383.6 $cm^{-1}$

## 33

1-Cyanopyrrole



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 0.0000000 | 0.0000000 | 0.3377412 |
| N | 0.0000000 | 0.0000000 | 2.8199254 |
| C | 0.0000000 | 0.0000000 | 1.6706890 |
| C | 0.0000000 | 1.1345100 | -0.4742498 |
| C | 0.0000000 | -1.1345100 | -0.4742498 |
| C | 0.0000000 | 0.7223813 | -1.7670273 |
| C | 0.0000000 | -0.7223813 | -1.7670273 |
| H | 0.0000000 | 2.1089129 | -0.0364309 |
| H | 0.0000000 | -2.1089129 | -0.0364309 |
| H | 0.0000000 | 1.3600696 | -2.6264107 |
| H | 0.0000000 | -1.3600696 | -2.6264107 |

CASSCF Reference energy: -300.6033328921
CASPT2 Total energy: -301.4601940408
Residual norm: 0.0000006654
Reference weight: 0.77949

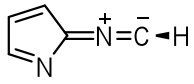
CAS(8,8) active space: 4 π/π* pairs.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation(a1,b1,a2,b2) | Coef | Weight |
|---|---|---|---|
| 111 | 0,220,20,20 | 0.947709 | 0.898152 |

## 36

*N*-(2*H*-pyrrol-2-ylidene)methanideiminium



Atom Coordinates (Angstroms)

| Type | X | Y | Z |
|---|---|---|---|
| N | -0.0970659 | 1.5836753 | -0.0364837 |
| N | -1.1280200 | -0.5115640 | -0.0091340 |
| C | -0.6697923 | -1.7319395 | -0.0018562 |
| C | 0.7831958 | -1.7903226 | 0.0003482 |
| C | 1.2099799 | -0.4964432 | -0.0071537 |
| C | 0.0005728 | 0.2866522 | -0.0126789 |
| C | -0.1999168 | 2.7595836 | 0.1162585 |
| H | -1.3368900 | -2.5731341 | 0.0027434 |
| H | 1.3821243 | -2.6791282 | 0.0077225 |
| H | 2.2121366 | -0.1176536 | -0.0062960 |
| H | -0.2699720 | 3.5674959 | -0.5825927 |

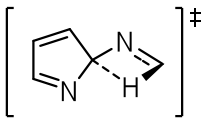
CASSCF Reference energy: -300.5562130329
CASPT2 Total energy: -301.3962691997
Residual norm: 0.0000001924
Reference weight: 0.78208

CAS(8,8) active space: 4 π/π* pairs.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | -0.921150 | 0.848517 |

## TS 36 → 40




Atom Coordinates (Angstroms)

| Type | X | Y | Z |
|---|---|---|---|
| N | -1.7300063 | -0.0213260 | -0.6455964 |
| N | 0.3336795 | -1.1711186 | 0.0015249 |
| C | 1.5541576 | -0.7568887 | 0.0010529 |
| C | 1.6730655 | 0.7134060 | 0.0125568 |
| C | 0.4127386 | 1.1926554 | 0.0268711 |
| C | -0.4608535 | 0.0015395 | 0.0106625 |
| C | -2.1483955 | -0.0727550 | 0.5432782 |
| H | 2.3756669 | -1.4482747 | -0.0034895 |
| H | 2.5905063 | 1.2667318 | 0.0043430 |
| H | 0.0671136 | 2.2059384 | 0.0233313 |
| H | -1.1509238 | -0.0555781 | 1.2690162 |

CASSCF Reference energy: -300.4900926661
CASPT2 Total energy: -301.3322257553
Residual norm: 0.0000002142
Reference weight: 0.78093

CAS(8,8) active space: 3 π/π* pairs and σ/σ* of new C-H bond.

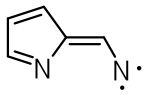
Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|

| | | | |
|---|---|---|---|
| 1 | 22220000 | -0.920689 | 0.847668 |

Imaginary frequency: -1267.3 $cm^{-1}$

## 38Z $T_0$



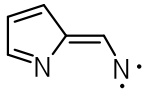
| Atom Type | X | Y | Z |
|---|---|---|---|
| N | -0.8730771 | -0.6866377 | 0.0000000 |
| N | -1.5807601 | 2.1291292 | 0.0000000 |
| C | -0.3554555 | 1.7269614 | 0.0000000 |
| C | -0.1644359 | -1.7769488 | 0.0000000 |
| C | 1.2875273 | -1.5057268 | 0.0000000 |
| C | 1.4013491 | -0.1533815 | 0.0000000 |
| C | 0.0407883 | 0.3535025 | 0.0000000 |
| H | -0.6255903 | -2.7460342 | 0.0000000 |
| H | 2.0669086 | -2.2407938 | 0.0000000 |
| H | 2.2935119 | 0.4399859 | 0.0000000 |
| H | 0.4167728 | 2.4827752 | 0.0000000 |

CASSCF Reference energy: -300.5624916983
CASPT2 Total energy: -301.3739483677
Residual norm: 0.0000008618
Reference weight: 0.79031

CAS(8,8) active space: 3 π/π* pairs and $p_y/p_z$ AO on nitrene N.

| Conf | Occupation(a',a") | Coef | Weight |
|---|---|---|---|
| 1 | u,222u000 | 0.910394 | 0.828817 |

## 38Z $S_1$



| Atom Type | X | Y | Z |
|---|---|---|---|
| N | -0.8658911 | -0.6566409 | 0.0000000 |
| N | -1.5756030 | 2.1698789 | 0.0000000 |
| C | -0.1328540 | -1.7980163 | 0.0000000 |
| C | 1.2908265 | -1.5243237 | 0.0000000 |
| C | 1.3978133 | -0.1707876 | 0.0000000 |
| C | 0.0109352 | 0.3289368 | 0.0000000 |
| C | -0.3792361 | 1.7555188 | 0.0000000 |
| H | -0.6111411 | -2.7564878 | 0.0000000 |
| H | 2.0746678 | -2.2537393 | 0.0000000 |

| | | | |
|---|---|---|---|
| H | 2.2843807 | 0.4311006 | 0.0000000 |
| H | 0.4115131 | 2.4942431 | 0.0000000 |

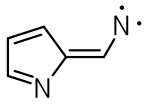
CASSCF Reference energy: -300.5488967669
CASPT2 Total energy: -301.3609718224
Residual norm: 0.0000002668
Reference weight: 0.79004

CAS(8,8) active space: 3 π/π* pairs and $p_y/p_z$ AO on nitrene N.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation(a',a") | Coef | Weight |
|---|---|---|---|
| 1 | u,222d000 | 0.925205 | 0.856005 |

## 38E $T_0$



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 1.3461130 | 0.0897509 | 0.0000000 |
| N | -1.7375361 | 1.9929451 | 0.0000000 |
| C | 1.4556728 | -1.2139317 | 0.0000000 |
| C | 0.1433269 | -1.8845378 | 0.0000000 |
| C | -0.7746362 | -0.8883070 | 0.0000000 |
| C | -0.0014451 | 0.3495468 | 0.0000000 |
| C | -0.4853142 | 1.6978672 | 0.0000000 |
| H | 2.4145653 | -1.6953505 | 0.0000000 |
| H | -0.0225468 | -2.9429566 | 0.0000000 |
| H | -1.8427945 | -0.9590618 | 0.0000000 |
| H | 0.2417826 | 2.4952504 | 0.0000000 |

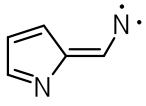
CASSCF Reference energy: -300.5665358313
CASPT2 Total energy: -301.3787410910
Residual norm: 0.0000001574
Reference weight: 0.79022

CAS(8,8) active space: 3 π/π* pairs and $p_y/p_z$ AO on nitrene N.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation(a',a") | Coef | Weight |
|---|---|---|---|
| 1 | u,222u000 | 0.911870 | 0.831506 |

## 38E $S_1$



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -0.8540757 | -0.6207003 | 0.0000000 |
| N | 0.4261477 | 2.7207865 | 0.0000000 |
| C | -0.1219586 | -1.7916987 | 0.0000000 |
| C | 1.2851312 | -1.5335441 | 0.0000000 |
| C | 1.4118843 | -0.1733118 | 0.0000000 |
| C | 0.0264903 | 0.3423053 | 0.0000000 |
| C | -0.3932084 | 1.7557637 | 0.0000000 |
| H | -0.6183665 | -2.7403332 | 0.0000000 |
| H | 2.0636292 | -2.2686918 | 0.0000000 |
| H | 2.3024595 | 0.4208628 | 0.0000000 |
| H | -1.4549316 | 1.9541350 | 0.0000000 |

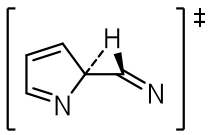
CASSCF Reference energy: -300.5547834683
CASPT2 Total energy: -301.3671333853
Residual norm: 0.0000003884
Reference weight: 0.78994

CAS(8,8) active space: 3 π/π* pairs and $p_y/p_z$ AO on nitrene N.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation(a',a") | Coef | Weight |
|---|---|---|---|
| 1 | u,222d000 | 0.924558 | 0.854808 |

## TS 38 → 32




| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 2.8913275 | -0.2333962 | -0.1326847 |
| N | -0.5589864 | -1.1184869 | -0.0798668 |
| C | -1.7711219 | 0.8387271 | 0.0331552 |
| C | -1.7618093 | -0.6215230 | -0.0683099 |
| C | 0.2821046 | -0.0156316 | -0.0610241 |
| C | 1.7039942 | -0.1767400 | 0.0579881 |
| C | -0.4681745 | 1.2182087 | 0.0917743 |
| H | -2.6398135 | 1.4654089 | 0.0421474 |
| H | -2.6239254 | -1.2574583 | -0.1265044 |
| H | 1.3045958 | -0.2707295 | 1.1487267 |
| H | -0.0515546 | 2.2025358 | 0.1503821 |

CASSCF Reference energy: -300.5078063937
CASPT2 Total energy: -301.3416083966
Residual norm: 0.0000001768
Reference weight: 0.78212

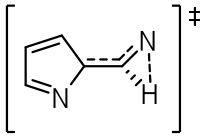
CAS(8,8) active space:
3 π/π* pairs and σ(overlapping with $p_z$ AO on nitrene N)/σ* of new C-H bond.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | 0.891288 | 0.794395 |

Imaginary frequency: -1610.3 $cm^{-1}$

## TS 38 → 39



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 2.8343613 | -0.2680772 | 0.2959342 |
| N | -0.5863904 | -1.1568670 | 0.1927304 |
| C | -1.7894203 | -0.6867157 | 0.0357583 |
| C | -1.8100796 | 0.7566822 | -0.1826279 |
| C | -0.5112180 | 1.1573346 | -0.1536918 |
| C | 0.2473275 | -0.0448144 | 0.1268458 |
| C | 1.6213511 | -0.1943658 | 0.1018731 |
| H | -2.6455914 | -1.3332807 | 0.0710143 |
| H | -2.6825414 | 1.3629137 | -0.3220803 |
| H | -0.1116063 | 2.1451312 | -0.2624753 |
| H | 2.0983490 | -0.4834029 | -0.9227817 |

CASSCF Reference energy: -300.4945838728
CASPT2 Total energy: -301.3320467591
Residual norm: 0.0000003598
Reference weight: 0.78175

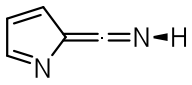
CAS(8,8) active space:
3 $\pi/\pi^*$ pairs and $\sigma$(overlapping with $p_z$ AO on nitrene N)/$\sigma^*$ of new N-H bond.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | 0.903347 | 0.816036 |

Imaginary frequency: -2001.1 $cm^{-1}$

## 39



| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 2.8251723 | -0.0330628 | -0.1542614 |
| N | -0.5033942 | -1.1699741 | -0.0060273 |

| | | | |
|---|---|---|---|
| C | -1.7301546 | -0.7620390 | 0.0197886 |
| C | -1.8531212 | 0.7009074 | 0.0280391 |
| C | -0.5893077 | 1.1828784 | 0.0067869 |
| C | 0.2772954 | 0.0032578 | -0.0231783 |
| C | 1.6048959 | -0.0348224 | -0.0160573 |
| H | -2.5465911 | -1.4596036 | 0.0335185 |
| H | -2.7699846 | 1.2554421 | 0.0437721 |
| H | -0.2597115 | 2.2018640 | -0.0011295 |
| H | 3.3387261 | -0.0552219 | 0.7124292 |

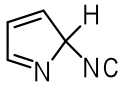
CASSCF Reference energy: -300.5914321861
CASPT2 Total energy: -301.4209687421
Residual norm: 0.0000002886
Reference weight: 0.78672

CAS(8,8) active space: 4 π/π* pairs.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | -0.923802 | 0.853409 |

## 40




| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | -0.4611233 | -1.1843430 | 0.1901369 |
| N | 1.6173492 | -0.0610017 | -0.0230447 |
| C | 0.3313092 | -0.0256756 | 0.5872963 |
| C | -1.5678671 | -0.7335672 | -0.2701712 |
| C | -1.6440968 | 0.7459484 | -0.2940566 |
| C | -0.4776591 | 1.1909550 | 0.1955907 |
| C | 2.6815775 | -0.0524309 | -0.5137417 |
| H | 0.4746175 | -0.0747003 | 1.6595644 |
| H | -2.3422922 | -1.3982982 | -0.6063904 |
| H | -2.4750043 | 1.3215208 | -0.6502520 |
| H | -0.1441379 | 2.1996794 | 0.3330382 |

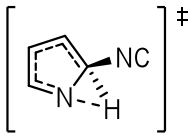
CASSCF Reference energy: -300.6166982998
CASPT2 Total energy: -301.4106696458
Residual norm: 0.0000004551
Reference weight: 0.79724

CAS(8,8) active space: 4 π/π* pairs.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | 0.931719 | 0.868100 |

## TS 40 → 41




| Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|
| N | 0.4105757 | -1.1530272 | -0.0128023 |
| N | -1.7266872 | -0.0109442 | -0.0097631 |
| C | -0.3549767 | 0.0350572 | 0.1590189 |
| C | 0.4673205 | 1.1695312 | 0.0655852 |
| C | 1.7601341 | 0.6795188 | -0.0978008 |
| C | 1.6833051 | -0.7145390 | -0.1163269 |
| C | -2.8930775 | -0.0054554 | -0.1358506 |
| H | -0.0181863 | -0.7692510 | 1.1011558 |
| H | 0.1381138 | 2.1863281 | 0.1180923 |
| H | 2.6581956 | 1.2611366 | -0.1594098 |
| H | 2.4862791 | -1.4222321 | -0.1338337 |

CASSCF Reference energy: -300.5253397988
CASPT2 Total energy: -301.3556110333
Residual norm: 0.0000004431
Reference weight: 0.78632

CAS(8,8) active space: 4 π/π* pairs.

Occupation of active orbitals, (u,d: Spin up or down):

| Conf | Occupation | Coef | Weight |
|---|---|---|---|
| 1 | 22220000 | -0.941610 | 0.886630 |

Imaginary frequency: -2439.5 $cm^{-1}$