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Supporting Information

69451 Weinheim, Germany

Photochemical Steps in the Prebiotic Synthesis of Purine Precursors from HCN**

*Eliot Boulanger, Anakuthil Anoop, Dana Nachtigallova, Walter Thiel, and Mario Barbatti**

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Computational details

Density functional theory (DFT) and time-dependent (TD) DFT[1] were applied using the CAM-B3LYP[2] and B3LYP[3] functionals. The aug-cc-pVDZ and aug-cc-pVTZ basis sets were adopted.[4] These calculations were done with Gaussian 09.[5] Due to convergence difficulties, two structures (CI-3 and TS 5-7 S_1) were optimized with the 6-31G* basis set. The search for intersections with TDDFT employed the penalty function approach[6] using a modified version of Chemshell.[7]

Complementary calculations were performed with the approximate second-order coupled-cluster CC2 method[8] using Turbomole[9] and with the complete-active-space second-order perturbation theory (CASPT2) in its multistate version (MS).[10] In the latter case, the CASSF and PT2 calculations were carried out with Columbus[11] and Molcas,[12] respectively. The active space consisted of 6 electrons in 10 π orbitals. The CASSCF treatment was averaged over 3 states and used the 6-311G** basis set.[13] A level shift of 0.3 and default IPEA corrections were adopted in the MS-CASPT2 calculations.

In the QM/MM setup, the structure of *trans*-DAMN was first optimized at the QM(B3LYP/6-31G**) level, including a first shell of 9 water molecules for microsolvation. The optimized cluster was embedded into a 100×100×100 Å^3 box of MM water molecules described by the TIP3P model.[14] Approximate MM parameters were derived for the DAMN molecule using CGenFF.[15] After heating the system up to 300 K, a 1 ns molecular dynamics (MD) simulation was run in the NPT ensemble to ensure a realistic density of the bulk, with the DAMN/9-water cluster being restrained in the center of the box to maintain its initial geometry. Once equilibrated, a sphere of water molecules was cut from the box, including every water molecule whose oxygen was located within 48 Å from the center-of-mass of the DAMN molecule.

QM/MM MD runs were performed with Chemshell.[7] The DAMN/9-water cluster and the surrounding water solvent molecules formed the QM and MM region, respectively. The QM part was treated with the OM2 semiempirical method[16] using the MNDO program,[17] while the MM part was described by the TIP3P water model using the DL-POLY code.[18] The system was heated up again and equilibrated for 500 ps with a 1 fs time step in the NVT ensemble to ensure a temperature of 300 K. Starting from the resulting coordinates and velocities, one reference MD simulation was run in the NVE ensemble. The second MD simulation in the NVE ensemble started from the same initial conditions, but in addition also included the photoenergy transferred to the vibrational modes (hot spot, see main paper).

Predominance of trans in the photostationary state

The predominance of the *trans* over the *cis* isomer in the photostationary state of DAMN can be understood from simple consideration of the potential energy surface. When *cis* is excited, it finds the twisted conical intersection (CI-1). There, it can either isomerize or remain as *cis*. For the sake of argument, we assume 50:50 chances for either channel. When *trans* is excited, it can either find the twisted conical intersection or relax to the S_1 minimum. We assume 50:50 chances for this split as well. At the twisted conical intersection, it can either isomerize into *cis* (25%) or remain as *trans* (25%). At the S_1 minimum, it should return to the ground state in a radiationless process near CI-2, therefore with *trans* structure; if AIAC (**5**) is populated, it may also occasionally return to *trans*. With these assumptions, the quantum yields are approximately $\Phi_{cis\rightarrow trans} = 0.5$ and $\Phi_{trans\rightarrow cis} = 0.25$. The estimated quantum-yield ratio $\Phi_{cis\rightarrow trans}/\Phi_{trans\rightarrow cis} = 2$ is in good qualitative agreement with the experimental quantum-yield ratio obtained from the data reported in Ref.[19]:

$$\frac{\Phi_{cis\rightarrow trans}}{\Phi_{trans\rightarrow cis}} = \frac{1}{q}\frac{\sigma_{trans}}{\sigma_{cis}} = 2.8\,,$$

where $q = 1/4$ is the observed photostationary ratio[19] and $\sigma_{trans}/\sigma_{cis} = 0.68$. The latter value is obtained by integrating the absorption spectra of *trans*- and *cis*-DAMN reported in Ref.[20] over the irradiation domain (280 nm – 315 nm).

Thermodynamic and spectroscopic data

As far as we know, there is only a single computational investigation of this photochemical reaction.[21] In that work, Bigot and Roux computed several reaction pathways for the rearrangement via isocyanide, azetene, and azirine intermediates, with the latter one being favored. Although several qualitative insights from Ref.[21] are still relevant, their quantitative results are of limited value due to the low level of the computational methods available at that time (CI/STO-3G). Therefore, in addition to our main focus on the photochemical rearrangement, we provide in this section more accurate computational results concerning the thermodynamics and spectroscopy of the HCN tetramers.

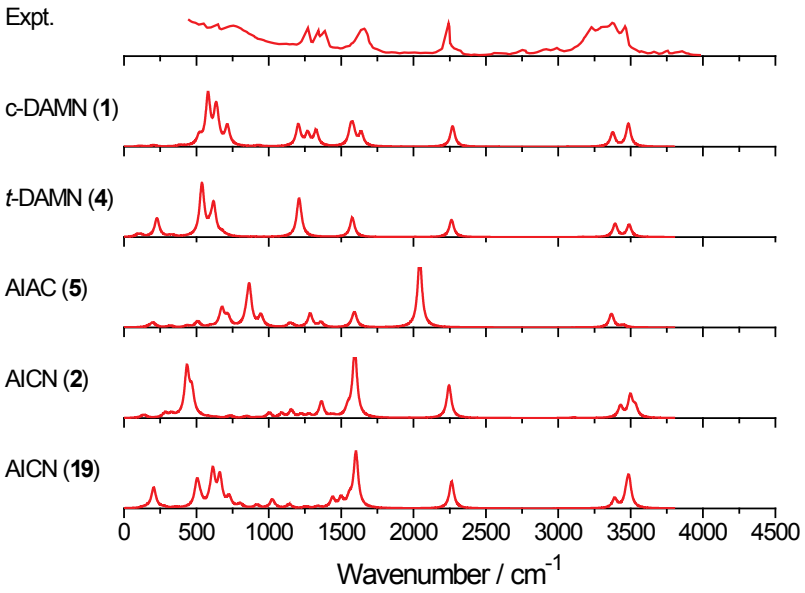

Figure 1. IR spectra of the main isomers of the HCN tetramer computed at the CAM-B3LYP/aug-cc-pVTZ level. Computational wavenumbers multiplied by 0.95 to account for anharmonic effects. Experimental spectrum (Fourier Transform Infrared Photoacoustic Spectroscopy) for *cis*-DAMN isomer from Ref.[22]. An intermediate with absorption in the 2000-2020 cm^{-1} region, detected in liquid film and KBr matrix, was reported in Ref.[23]. AIAC (**5**) is a good candidate for this intermediate (2045 cm^{-1} in the gas-phase simulation).

Table 1. Vertical excitation energies and oscillator strengths of the main isomers of the HCN tetramer. The numbers in brackets are the ground-state energy shifts relative to the *cis*-DAMN minimum. Bright states are indicated in bold.

	CC2 aug-cc-pVDZ		TD-B3LYP aug-cc-pVDZ		TD-CAM-B3LYP aug-cc-pVDZ		TD-CAM-B3LYP aug-cc-pVTZ	
Assignment	ΔE (eV)	*f*	ΔE (eV)	*f*	ΔE (eV)	*f*	ΔE (eV)	*f*
cis-DAMN (**1**)								
cs	0.00	-	0.00	-	0.00	-	0.00	-
π_{CC}-Ryd($3s_+(NH_2)$)	4.73	0.021	4.37	0.063	4.79	0.013	4.82	0.015
π_{CC}-π^*_{CC}	**4.91**	**0.416**	**4.45**	**0.285**	**4.63**	**0.374**	**4.71**	**0.373**
π_{CC}-Ryd($3s_-(NH_2)$)	5.69	0.001	5.37	0.002	5.84	0.002	5.86	0.002
π_{CC}-σ^*_{CN}	5.84	0.006	5.22	0.013	5.63	0.011	5.68	0.010
trans-DAMN (**4**)	[+0.03]		[+0.02]		[+0.02]		[+0.02]	
cs	0.00	-	0.00	-	0.00	-	0.00	-
π_{CC}-π^*_{CC}	**4.37**	**0.307**	**3.93**	**0.247**	**4.15**	**0.286**	**4.21**	**0.281**
π_{CC}-σ^*_{CN}	5.13	0.001	4.45	0.002	4.92	0.002	4.96	0.001
π_{CC}-Ryd($3s_+(NH_2)$)	5.00	0.015	4.75	0.012	5.14	0.013	5.13	0.014
π_{CC}-σ^*_{CN}	5.89	0.002	5.41	0.003	5.87	0.002	5.88	0.002
AICN (**2**)	[-0.86]		[-0.93]		[-1.06]		[-1.05]	
cs	0.00	-	0.00	-	0.00	-	0.00	-
π_{CC}-Ryd(3s(NH))	5.08	0.010	4.72	0.002	5.13	0.008	5.14	0.010
π_{CC}-π^*_{CC}	**5.25**	**0.189**	**4.84**	**0.183**	**5.18**	**0.206**	**5.18**	**0.215**

Table 2. Energies (eV) of experimental band maxima in diverse solvents. Wavelengths in nm are given in parenthesis.

Solvent	*cis*-DAMN	*trans*-DAMN	AICN
EPA [20]	4.19 (296)	3.95 (314)	4.96-5.06 (245-250)
Methanol [19]	4.16 (298)	3.96 (313)	4.96 (250)
Ethanol [24]	4.20 (295)		
Water [25]	4.20 (295)		
Water [24]	4.13 (300)		
Water [26]		4.00 (310)	
Water pH 6.8 [27]			5.04 (246)
Ethyl ether [28]	4.29 (289)		
Benzene [25]	4.32 (287)		
MeCN [25]	4.22 (294)		
MeCN [26]	4.20 (296)	4.07-4.08 (304-305)	
0.1 N HCl [24]	4.28 (290)		
0.1 N HCl [25]	4.23 (293)		
1 N HCl [25]	4.38 (283)		
6 N HCl [25]	4.41 (281)		

Table 3. Gibbs free energies (298 K) computed at the CAM-B3LYP/aug-cc-pVTZ level for different minima (Min) and transition states (TS). ΔG is the free energy difference between TS and the reactant.

Structure	State	Feature	*G* / hartree	ΔG / kcal/mol
4	S_0	Min	-373.698610	
5	S_0	Min	-373.655996	
7	S_0	Min	-373.659397	
8	S_0	Min	-373.627543	
10	S_0	Min	-373.592235	
11	S_0	Min	-373.668608	
12	S_0	Min	-373.619161	
13	T_1	Min	-373.643621	
14	S_0	Min	-373.616633	
15	S_0	Min	-373.655673	
17	S_0	Min	-373.686475	
18	S_0	Min	-373.617269	
4-5	S_0	TS	-373.615867	52
4-10	S_0	TS	-373.579970	74
4-11	S_0	TS	-373.614892	53
4-14	S_0	TS	-373.577031	76
5-7	S_0	TS	-373.618298	24
5-15	S_0	TS	-373.612976	27
7-15	S_0	TS	-373.627755	20
7-18	S_0	TS	-373.531773	80
8-2	S_0	TS	-373.562311	41
8-12	S_0	TS	-373.562312	41
10.8	S_0	TS	-373.584977	5
10-14	S_0	TS	-373.590922	1
11-12	S_0	TS	-373.592405	48
12-2	S_0	TS	-373.613946	3
13-16	T_1	TS	-373.549912	59
14-2	S_0	TS	-373.584432	20
15-17	S_0	TS	-373.572514	52
17-2	S_0	TS	-373.618221	43
17-19	S_0	TS	-373.622019	40
18-19	S_0	TS	-373.606446	7

Table 4. Ground- and excited-state energies for several 4HCN isomers. Bright states in bold. (TD)CAM-B3LYP/aug-cc-pVTZ level.

			Relative energy / eV				Absolute energy / eV				
Isomer	Optim.	S_0 / au	S_1	S_2	S_3	S_4	S_0	S_1	S_2	S_3	S_4
1	S_0	-373.751467	**4.710**	4.818	5.677	5.856	0.000	**4.710**	4.818	5.677	5.856
2	S_0	-373.790109	5.139	**5.175**	5.303	5.683	-1.052	4.087	**4.123**	4.251	4.631
4	S_0	-373.750620	**4.206**	4.963	5.127	5.876	0.023	**4.229**	4.986	5.150	5.899
4	S_1-1	-373.685902	1.567	**3.282**	4.224	4.562	1.784	3.351	**5.066**	6.008	6.346
4	S_1-2	-373.692061	1.540	**3.401**	4.218	4.524	1.617	3.157	**5.018**	5.835	6.141
5	S_0	-373.706410	4.455	**4.606**	4.702	5.505	1.226	5.681	**5.832**	5.928	6.731
5	S_1	-373.663153	1.351	3.079	3.957	4.461	2.403	3.754	5.482	6.360	6.864
7	S_0	-373.713182	3.701	5.047	5.122	5.264	1.042	4.743	6.089	6.164	6.306
7	S_1	-373.676652	1.796	3.880	3.950	4.554	2.036	3.832	5.916	5.986	6.590
8	S_0	-373.678342	4.720	5.295	5.505	5.597	1.990	6.710	7.285	7.495	7.587
10	S_0	-373.640913	0.568	2.910	4.029	4.334	3.008	3.576	5.918	7.037	7.342
11	S_0	-373.719901	**4.398**	5.004	5.121	5.500	0.859	**5.257**	5.863	5.980	6.359
11	S_1	-373.660020	1.474	**3.539**	4.125	4.566	2.488	3.962	**6.027**	6.613	7.054
12	S_0	-373.667773	**3.214**	3.269	4.606	4.658	2.277	**5.491**	5.546	6.883	6.935
13	T_1	-373.650067	0.221	3.422	3.813	4.355	2.759	2.980	6.181	6.572	7.114
14	S_0	-373.659951	3.346	4.627	5.157	6.118	2.490	5.836	7.117	7.647	8.608
15	S_0	-373.709616	3.638	4.875	5.113	5.226	1.139	4.777	6.014	6.252	6.365
15	S_1	-373.669713	1.590	3.575	3.855	4.519	2.225	3.815	5.800	6.080	6.744
16	T_1	-373.635412	0.221	3.422	3.813	4.355	3.158	3.379	6.580	6.971	7.513
17	S_0	-373.743354	5.109	5.418	5.461	**5.546**	0.221	5.330	5.639	5.682	**5.767**
18	S_0	-373.667798	3.285	3.938	4.930	5.073	2.277	5.562	6.215	7.207	7.350
19	S_0	-373.784626	5.030	**5.641**	**5.814**	**6.055**	-0.902	4.128	4.739	**4.912**	**5.153**

CASPT2 data

The main reaction paths determined with TDDFT have been checked with CASPT2 using geometries optimized at the CASSCF level. All main qualitative features discussed in the text were also found at the CASPT2//CASSCF level. A summary of these results is given in Table 5. The CASPT2 energy split between S_1 and S_0 is due to the fact that the energy (MS-CASPT2) was not computed at the same level at which the geometry was optimized (SA-CASSCF).

Table 5. Comparison between CASPT2//CASSCF and TDDFT energies.

Structure	Method	S_0 / eV	S_1 / eV
1-S_0	CASPT2	0.00	4.98
	TDDFT	0.00	4.71
4-S_0	CASPT2	0.02	4.55
	TDDFT	0.02	4.23
4-S_1	CASPT2	1.79	3.58
	TDDFT	1.62	3.16
CI-1	CASPT2	2.87	3.00
	TDDFT	2.77	2.80
CI-2	CASPT2	3.15	3.25
	TDDFT	3.96	3.98
CI-3	CASPT2	4.45	4.84
	TDDFT	4.79	4.83

Final tautomerization

We have tested the impact of solvation on the reaction barrier for the final tautomerization, NHC (**17**) → AICN (**2** or **19**) (Table 6). The gas-phase barrier of about 40 kcal/mol is quite large. We have investigated two other setups to assess the feasibility of this process. First, when a molecule of water is introduced to serve as a bridge for the H transfer and a polarizable continuum model is used to simulate the bulk solvent, the barrier is reduced to 13 kcal/mol. Secondly, when the dimer of **17** in the gas phase is taken to represent the limiting case of a very high HCN concentration, the barrier is lowered to only 3 kcal/mol.

Table 6. NHC → AICN tautomerization barriers in the gas phase and in water. Calculations in water include one explicit water molecule plus the polarizable continuum model (PCM).[29]

Reaction	Phase	ΔG / kcal/mol
17 → 2	Gas[a]	43
17 → 19	Gas[a]	40
17 → 2	Water[b]	15
17 → 19	Water[b]	13
17:17 → 2:2	Dimer[c]	3
17:17 → 2:19	Dimer[c]	4
17:17 → 19:19	Dimer[c]	4

[a] TD-CAM-B3LYP/aug-cc-pVTZ.

[b] TD-CAM-B3LYP/aug-cc-pVTZ//CAM-B3LYP/cc-pVTZ + PCM.

[c] TD-CAM-B3LYP/cc-pVTZ.

Reaction paths

Energy barriers in the first excited state were estimated by computing the energy profile between reactant and product using linear interpolation of internal coordinates (LIIC). The barriers are given as the difference between the maximum of the ground-state energy and the S_1 minimum energy of the reactant. This supposes that internal conversion is possible along the reaction pathway. If this is not the case, the barriers would be even larger. The calculations were performed at the TD-CAM-B3LYP/aug-cc-pVTZ level. In each diagram, the dotted line indicates 4 eV energy excess above the ground state of the nearest structure that could have been photoexcited.

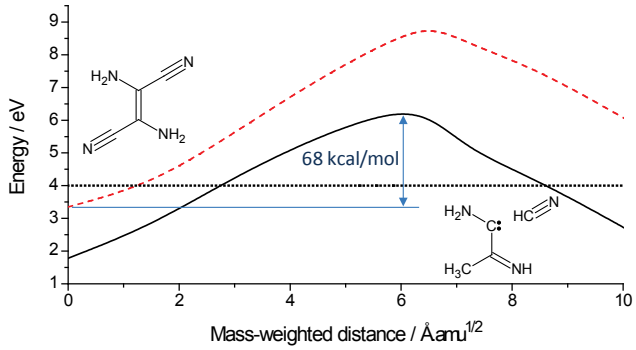

Figure 2. Energy profile for the ground and first excited state along the LIIC pathway between the S_1 minimum of *trans*-DAMN (**4**) and the ground-state minimum of **14**.

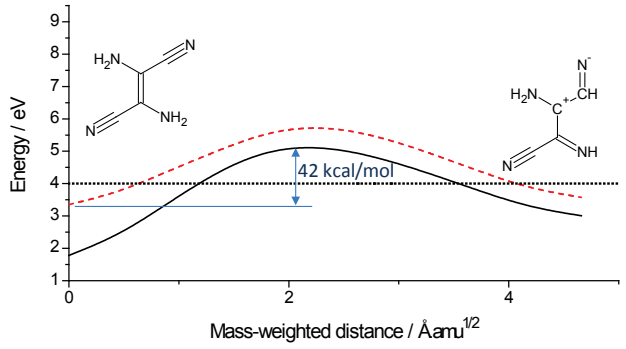

Figure 3. Energy profile for the ground and first excited state along the LIIC pathway between the S_1 minimum of **4** and the ground-state minimum of **10**.

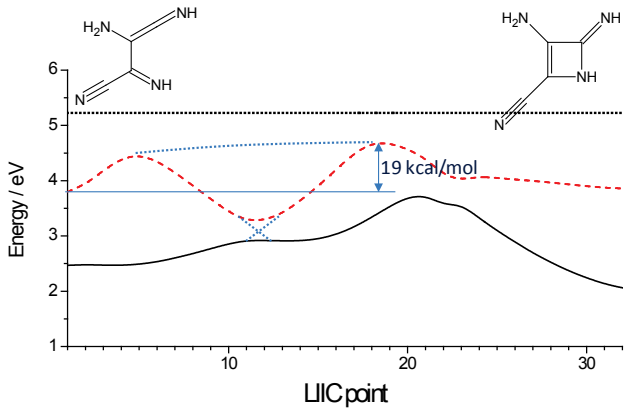

Figure 4. Energy profile for the ground and first excited state along the LIIC pathway between the twisted S_1 minimum of **5** and the S_1 minimum of **7**. The crossing lines around LIIC point 11 indicate a state crossing at the planar geometry. The dotted line connecting the two maxima illustrates an alternative path not involving the crossing.

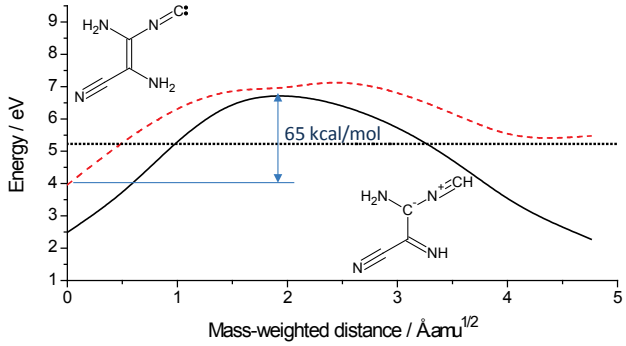

Figure 5. Energy profile for the ground and first excited state along the LIIC pathway between the S_1 minimum of **11** and the ground-state minimum of **12**.

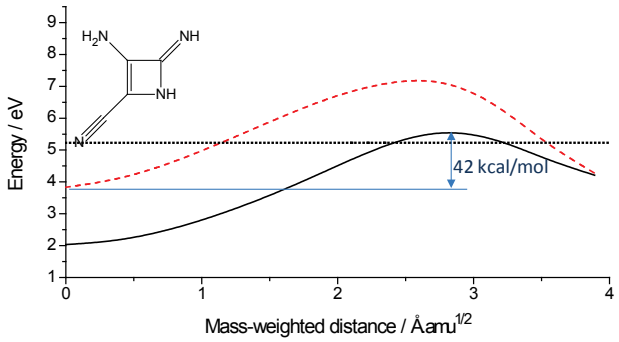

Figure 6. Energy profile for the ground and first excited state along the LIIC pathway between the S_1 minimum of **7** and the S_1/S_0 intersection that leads to **18**.

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Cartesian coordinates

Cartesian coordinates (Å) of geometries optimized at the (TD)-CAM-B3LYP/aug-cc-pVTZ level, unless indicated otherwise.

S_0 minima

```
12
1 MIN S0
 C          0.429524        0.085923       -0.515699
 C         -0.523133       -0.085657        0.421684
 C          0.113861        0.173826       -1.900460
 C         -1.907651       -0.094144        0.093096
 N         -0.075276        0.247278       -3.028565
 N         -3.036242       -0.106043       -0.106730
 N          1.775735        0.118869       -0.160776
 N         -0.181959       -0.197422        1.767214
 H          1.964950        0.632054        0.688772
 H          2.402867        0.373594       -0.905511
 H         -0.943175       -0.445872        2.376831
 H          0.641210       -0.757916        1.937902
12
2 MIN S0
 C         -0.427104        0.006094        0.345610
 C          0.421696        0.037452       -0.742237
 C          1.550464        0.102813        1.136808
 C          0.149365        0.023388       -2.117218
 N          0.291629        0.049060        1.498624
 N         -0.100820        0.015921       -3.239248
 N         -1.786694       -0.103302        0.364716
 N          1.698938        0.098501       -0.194029
 H         -2.290771        0.154430       -0.465125
 H         -2.224907        0.147297        1.233674
 H          2.560553        0.132849       -0.708268
 H          2.387740        0.147167        1.812764
12
4 MIN S0
 C          0.482729       -0.008040       -0.472197
 C         -0.482633       -0.008340        0.472611
 C          0.078453        0.024230       -1.840041
 C         -0.078362        0.023334        1.840470
 N         -0.284093        0.078579       -2.926511
 N          0.284175        0.077216        2.926966
 N          1.846616       -0.131208       -0.232219
 N         -1.846501       -0.131599        0.232573
 H          2.124524       -0.032418        0.732000
 H          2.440562        0.380941       -0.863657
 H         -2.440525        0.380150        0.864262
 H         -2.124425       -0.032385       -0.731597
12
5 MIN S0
 C          0.538826        0.004762       -0.594362
 C         -0.518717        0.086377        0.414037
 C          0.179342       -0.018854       -1.870721
 C         -0.044120        0.254403        1.782131
 N         -0.131355        0.093152       -3.023269
 N          0.295511        0.384008        2.867689
 N          1.922935       -0.056087       -0.284321
 N         -1.756392        0.016431        0.139062
 H          2.172690       -0.827830        0.315311
 H          2.293596        0.804310        0.090793
 H         -2.341942        0.110807        0.961888
 H         -0.359625       -0.724159       -3.579218
12
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7 MIN S0
 C         0.395480      -0.046549      -0.331749
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 C        -0.273748       0.052658       2.127728
 N        -0.969587      -0.212924      -2.434887
 N        -0.133851       0.125462       3.265817
 N         1.705215      -0.092742      -0.616329
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 H         2.391281       0.085644       0.093934
 H         1.988143       0.002136      -1.574809
 H        -2.338795       0.524645      -0.000635
 H        -1.948653      -0.304719      -2.695890
12
10 MIN S0
 C         0.445453       0.075414      -0.471051
 C        -0.565084      -0.023128       0.582424
 C         0.116189       0.418554      -1.902720
 C        -0.152152       0.358956       1.916309
 N         1.063747       0.452112      -2.702767
 N         0.192203       0.619845       2.975433
 N         1.689177      -0.164214      -0.264682
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 H         2.101096      -0.395877       0.624694
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 H        -2.371089      -0.386268       1.070389
 H        -0.960005       0.559013      -2.079853
12
11 MIN S0
 C         0.162334      -0.080216       1.297712
 C         0.114140      -0.046346      -0.048340
 C        -2.025150      -0.309231       2.570388
 C         1.348561       0.013911      -0.753763
 N        -1.018867      -0.192448       1.995318
 N         2.361033       0.036012      -1.292758
 N         1.288847       0.081636       2.084659
 N        -1.056818       0.036906      -0.805128
 H         2.163694       0.069278       1.584068
 H         1.304172      -0.479277       2.921556
 H        -1.024840      -0.467377      -1.676707
 H        -1.899366      -0.158979      -0.287795
12
12 MIN S0
 C         0.424848       0.138038      -0.524142
 C        -0.585579       0.114527       0.531319
 C        -0.367407       0.802938      -2.772947
 C        -0.072137      -0.024738       1.883681
 N         0.033391       0.368404      -1.712586
 N         0.332887      -0.127247       2.949540
 N         1.763854      -0.159576      -0.247895
 N        -1.827024       0.224809       0.284232
 H         2.027171      -0.048579       0.718756
 H         2.418488       0.293097      -0.866695
 H        -2.387640       0.219824       1.130149
 H        -0.732322       0.095072      -3.521572
12
14 MIN S0
 C        -0.865607       0.199390      -0.090126
 C         0.309561       0.080941      -0.938665
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 N        -0.141658      -0.018340      -3.491146
 N        -1.053037      -0.764490       0.741546
 N         1.489804       0.119029      -0.455300
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 H        -1.802628      -0.714364       1.416883
 H         2.201899       0.181986      -1.177101
 H         1.895701       0.053888       1.634430
12
15 MIN S0
 C         0.423813      -0.050216      -0.354413
 C        -0.414386      -0.004161       0.696427
 C        -0.781615      -0.151046      -1.243398
 C        -0.269431       0.053230       2.091060
 N        -1.094539      -0.140064      -2.449713
 N        -0.128349       0.124417       3.228673
 N         1.751050      -0.146503      -0.587775
 N        -1.638786      -0.214721      -0.091061
 H         2.386973       0.035783       0.169354
 H         2.091303       0.092732      -1.501856
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 H        -0.286839      -0.088720      -3.062894
12
17 MIN S0
 C         0.587212      -0.017244      -0.376887
 C        -0.347599       0.229170       0.579532
 C        -1.474232      -0.075890      -1.396828
 C        -0.164825       0.458560       1.950746
 N        -0.116089      -0.196167      -1.540979
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 N         1.954840      -0.032557      -0.317634
 N        -1.581935       0.188399      -0.091556
 H         2.344225       0.017823       0.609728
 H         2.419257      -0.710085      -0.899579
 H        -2.465284       0.344117       0.358785
 H         0.309203      -0.362057      -2.435312
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18 MIN S0
 C         0.906389       0.843595      -0.070030
 C        -0.262514       0.150911       0.430605
 C        -1.308324       0.098762      -1.608489
 C        -0.258508      -0.059210       1.863663
 N        -1.876189      -0.603781      -2.484674
 N        -0.176374      -0.238232       2.991007
 N         1.964756       0.153438      -0.316238
 N        -1.294655      -0.193769      -0.239263
 H         2.044353      -0.853958      -0.194567
 H         2.796356       0.613795      -0.658631
 H        -0.813844       1.028452      -1.902814
 H        -2.299864      -1.428413      -2.059789
12
19 MIN S0
 C         0.522724      -0.042711      -0.359899
 C        -0.397335       0.095181       0.649387
 C        -1.539445      -0.225363      -1.116562
 C        -0.082120       0.315470       2.010570
 N        -0.216169      -0.248103      -1.484442
 N         0.250426       0.489383       3.095013
 N         1.895999       0.066660      -0.378047
 N        -1.679672      -0.017538       0.149890
 H         2.292028       0.245029       0.532166
 H         2.384980      -0.678006      -0.850446
 H        -2.333769      -0.375971      -1.827325
 H         0.145953      -0.320852      -2.418614
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S_0 Transition states

```
12
4-5 TS S0
 C         0.641231       0.160935      -0.682194
 C        -0.461075       0.228866       0.249126
 C         0.025529       0.041099      -1.891494
 C        -0.075925       0.258227       1.642538
 N        -0.985090       0.018072      -2.504754
 N         0.212285       0.285355       2.749875
 N         1.990727      -0.059136      -0.370860
 N        -1.712237       0.169876      -0.087876
 H         2.177480      -0.898171       0.156343
 H         2.453676       0.731372       0.049067
 H        -2.351907       0.149265       0.694254
 H        -1.730243      -0.272620      -1.732714
12
4-10 TS S0
 C         0.484626       0.092740      -0.387488
 C        -0.497030      -0.039701       0.610972
 C        -0.178375       0.259657      -1.743627
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 N         0.226330       0.497146      -2.841771
 N         0.141910       0.668255       3.009242
 N         1.783766      -0.113396      -0.281720
 N        -1.705905      -0.406156       0.262547
 H         2.194453      -0.651715       0.461446
 H         2.392500       0.248873      -1.001023
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12
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4-11 TS S0
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N 1.335303 -0.036369 2.038563
N -1.090536 -0.087271 -0.729193
H 1.861784 -0.895096 2.044899
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H -1.010848 -0.170499 -1.725996
H -1.855744 -0.578586 -0.301293
12
4-14 TS S0
C 0.512696 -0.001512 -0.687613
C -0.475634 0.239540 0.278475
C 0.172508 0.415919 -2.023442
C 0.442510 0.301255 1.832502
N -0.091339 0.696168 -3.101917
N 0.066863 0.494439 2.917774
N 1.705200 -0.410568 -0.353070
N -1.709902 -0.177373 0.296110
H 1.365138 -0.023092 1.180341
H 2.408996 -0.198855 -1.053924
H -2.368614 0.249704 0.931548
H -2.031573 -0.994586 -0.202672
12
5-7 TS S0
C 0.594307 -0.109556 -0.392565
C -0.370875 -0.051057 0.594494
C -0.282001 -0.191882 -1.492572
C -0.187675 0.375050 1.948101
N -0.552858 -0.001847 -2.653569
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N 1.972388 -0.277159 -0.406100
N -1.535549 -0.403132 0.037035
H 2.362528 -0.683136 0.427944
H 2.507127 0.514732 -0.726524
H -2.338201 0.121875 0.381309
H -1.397641 -0.376713 -3.061189
12
5-15 TS S0
C 0.631281 -0.086585 -0.405835
C -0.354477 -0.032159 0.570195
C -0.219891 -0.211713 -1.523063
C -0.204459 0.410517 1.924282
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H 2.395041 -0.851650 0.277524
H 2.541745 0.637201 -0.452459
H -2.329723 0.073613 0.320649
H -0.073148 0.250190 -3.408558
12
7-15 TS S0
C 0.420875 -0.087357 -0.327383
C -0.417658 -0.015303 0.720351
C -0.783607 -0.251963 -1.229573
C -0.273836 0.104980 2.109852
N -1.013853 -0.301261 -2.416892
N -0.140674 0.228126 3.244466
N 1.741543 -0.148350 -0.581368
N -1.645865 -0.283996 -0.049463
H 2.401867 0.100316 0.133556
H 2.039266 -0.019792 -1.532046
H -2.343008 0.454460 -0.040052
H -1.173620 -0.353901 -3.390637
12
7-18 TS S0
C 0.305839 -0.024815 -0.277167
C -0.507715 -0.218105 0.825893
C -0.976864 0.059231 -1.107804
C -0.285043 -0.122558 2.216642
N -1.013961 -0.350439 -2.337745
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12
8-2 TS S0
C 0.611085 0.476560 0.060157
C -0.417287 -0.559819 0.163160
C 2.206757 -0.770499 -0.133182
C -1.737078 -0.065840 -0.182737
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N 0.319809 1.717748 0.447285
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H -1.060226 -2.335906 0.243096
H 3.290431 -0.907762 -0.040095
12
8-12 TS S0
C 0.486081 -0.591214 -0.396653
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H -1.127732 1.852231 1.073163
H 0.801023 0.927710 -2.985383
12
10-8 TS S0
C 0.482149 0.207922 -0.509900
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C 0.024055 0.363655 -1.917016
C -0.112860 0.216853 1.894681
N 0.705992 -0.305247 -2.701969
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H 2.410556 0.211564 -0.965051
H -2.348762 -0.334928 0.994981
H -0.937126 0.874733 -2.073482
12
10-14 TS S0
C 0.147202 -0.181597 -0.663381
C -0.728066 -0.156997 0.502329
C 0.075466 0.561988 -2.394192
C -0.127803 0.271982 1.752978
N 1.054586 0.274476 -3.002727
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H -0.858407 1.096448 -2.483217
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11-12 TS S0
C 0.104320 0.011790 1.426126
C -0.020617 0.054141 0.039111
C -2.180345 -0.193922 1.473828
C 1.153110 -0.090130 -0.761144
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H 2.116769 0.148396 1.637544
H 1.313857 -0.537018 2.957715
H -1.281970 -0.083020 -1.480403
H -2.273109 -0.696824 0.407340
12
12-2 TS S0
C 0.457201 0.037733 -0.428446
C -0.527196 0.058883 0.634924
C -1.123671 0.607059 -2.091324

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 N        -0.076438       0.219314      -1.582353
 N         0.379717      -0.000153       3.059461
 N         1.817943      -0.174639      -0.231753
 N        -1.771122       0.146276       0.340392
 H         2.109426      -0.154684       0.732297
 H         2.417135       0.386563      -0.816348
 H        -2.365862       0.239473       1.156757
 H        -1.768100      -0.079666      -2.641912
12
14-2 TS S0
 C         0.338014       0.120289      -0.606280
 C        -0.758786       0.435188       0.207597
 C         0.041194       0.400143      -1.997563
 C         1.249040       0.044393       1.944793
 N        -0.166047       0.566171      -3.111491
 N         0.102715       0.167096       2.027509
 N         1.535568      -0.228153      -0.252390
 N        -1.955190      -0.077922       0.178225
 H         2.291684      -0.054967       2.134313
 H         2.201203      -0.141587      -1.012376
 H        -2.729340       0.427802       0.577201
 H        -2.147035      -1.035003      -0.087837
12
15-17 TS S0
 C         0.899909       0.002469      -0.523368
 C        -0.205353       0.056183       0.251051
 C        -1.545448      -0.146797      -1.673403
 C        -0.274443      -0.012715       1.649534
 N        -0.900036       0.113441      -2.657808
 N        -0.254627      -0.048467       2.801901
 N         2.119122       0.188866      -0.032704
 N        -1.522440      -0.023392      -0.410951
 H         2.302476       0.446676       0.929370
 H         2.922542       0.056854      -0.617160
 H        -2.358635      -0.024290       0.150975
 H        -0.670007      -0.575399      -3.363027
12
17-2 TS S0
 C         0.552687      -0.099895      -0.402796
 C        -0.379528       0.216129       0.543334
 C        -1.479866      -0.328067      -1.343168
 C        -0.198464       0.514458       1.905440
 N        -0.115607      -0.486640      -1.548670
 N        -0.021910       0.764094       3.012245
 N         1.912226      -0.078305      -0.350264
 N        -1.617523       0.128396      -0.091217
 H         2.347795      -0.017784       0.553675
 H         2.385726      -0.660424      -1.019219
 H        -2.496062       0.368651       0.332967
 H        -0.820904       0.220857      -2.309608
12
17-19 TS S0
 C         0.527540      -0.026390      -0.310411
 C        -0.371067       0.143094       0.712868
 C        -1.567520      -0.269565      -1.140579
 C        -0.054665       0.385844       2.064744
 N        -0.220824      -0.214408      -1.432334
 N         0.272793       0.583812       3.147177
 N         1.881348      -0.004808      -0.300919
 N        -1.653841      -0.042874       0.207609
 H         2.336029      -0.034063       0.595665
 H         2.384867      -0.432894      -1.056368
 H        -2.208764       0.728032      -0.614325
 H         0.145916      -0.330130      -2.360926
12
18-19 TS S0
 C         0.668832       0.294663      -0.529233
 C        -0.410252       0.189603       0.356817
 C        -1.771647       0.286573      -1.364850
 C        -0.092409       0.180518       1.761653
 N        -0.870910      -0.097704      -2.207445
 N         0.235767       0.118601       2.856893
 N         1.777318      -0.378828      -0.506124
 N        -1.668306       0.262934      -0.015786
 H         1.920924      -1.219780       0.042073
 H         2.569764      -0.063411      -1.043916
 H        -2.659501       0.778107      -1.751159
 H        -0.277981      -0.839696      -1.848144
```

Triplet structures

```
12
13 MIN T1
 C         0.493692       0.149972      -0.541527
 C        -0.493620       0.149637       0.542017
 C         0.346007       0.990247      -1.644225
 C        -0.346072       0.989417       1.645111
 N         0.216177       1.681810      -2.561392
 N        -0.216354       1.680571       2.562603
 N         1.535841      -0.743954      -0.503521
 N        -1.535625      -0.744439       0.503590
 H         1.768200      -1.150171       0.386735
 H         2.303061      -0.615723      -1.141885
 H        -2.302866      -0.616633       1.142014
 H        -1.767918      -1.150275      -0.386857
12
16 MIN T1
 C         0.532075       0.517377      -0.525616
 C        -0.461824       0.452260       0.610985
 C         0.794882       1.654110      -1.278274
 C        -0.971013       1.785866       0.970916
 N         1.021008       2.586608      -1.923238
 N        -1.424986       2.790638       1.273579
 N         1.270786      -0.623410      -0.743325
 N        -1.504753      -0.512562       0.291835
 H         0.073892       0.069258       1.483024
 H         0.830942      -1.284772      -1.389306
 H        -2.040979      -0.758617       1.112638
 H        -2.140324      -0.149145      -0.406279
12
13-16 TS T1
 C         0.586580       0.334398      -0.654176
 C        -0.228464      -0.032253       0.525551
 C         0.284752       1.104538      -1.762229
 C        -0.112438       0.815023       1.697380
 N         0.014659       1.725095      -2.700168
 N        -0.004948       1.444417       2.647525
 N         1.750791      -0.363394      -0.362331
 N        -1.503179      -0.544041       0.327023
 H         0.827289      -0.834004       0.691700
 H         2.037123      -1.074856      -1.035579
 H        -2.004125      -0.869805       1.137010
 H        -1.647517      -1.084660      -0.509045
```

S_1 minima

```
12
4 MIN S1-1
 C         0.496537       0.049262      -0.554514
 C        -0.460288       0.043856       0.462218
 C         0.105358       0.053634      -1.919384
 C         0.014694       0.039380       1.895065
 N        -0.275247       0.056891      -3.002027
 N        -0.766786       0.035375       2.810949
 N         1.796593       0.050447      -0.220325
 N        -1.752906       0.042582       0.238233
 H         1.994889       0.046035       0.775162
 H         2.525968       0.052694      -0.908825
 H        -2.332224       0.038751       1.072299
 H        -2.170525       0.045487      -0.679097
12
4 MIN S1-2
 C         0.480889       0.083537      -0.511684
 C        -0.518588       0.107662       0.471037
 C         0.110419       0.010492      -1.885998
 C        -0.187015       0.182973       1.928657
 N        -0.283197      -0.049049      -2.962561
 N         0.932443       0.229663       2.376784
 N         1.766291       0.129292      -0.158525
 N        -1.801310       0.064817       0.164860
 H         1.933577       0.181212       0.861247
 H         2.499741       0.112296      -0.843066
 H        -2.451197       0.086356       0.937464
 H        -2.145548       0.012746      -0.780630
12
5 MIN S1
```

```
 C         0.658400       0.273935      -0.485696
 C        -0.351481       0.215006       0.588705
 C         0.327985      -0.388647      -1.620663
 C        -0.541235      -1.047024       1.192683
 N        -0.112085      -0.935553      -2.585735
 N        -0.688067      -2.078278       1.692272
 N         1.789812       0.963878      -0.323366
 N        -1.082898       1.307749       0.733635
 H         1.904333       1.475810       0.535895
 H         2.437335       1.120652      -1.077872
 H        -1.857657       1.136355       1.365743
 H        -0.233680      -1.916558      -2.796591
12
7 MIN S1
 C         0.397348      -0.071827      -0.423072
 C        -0.435356      -0.025974       0.757552
 C        -0.738900      -0.101045      -1.266257
 C        -0.291666       0.107026       2.127934
 N        -0.989216      -0.192608      -2.523721
 N        -0.136965       0.215676       3.267789
 N         1.712743      -0.101280      -0.622316
 N        -1.557152      -0.085010      -0.023600
 H         2.352087       0.021492       0.141943
 H         2.071159      -0.059624      -1.560191
 H        -2.488230       0.249247       0.184009
 H        -1.977639      -0.245707      -2.731526
12
11 MIN S1
 C         0.072283      -0.085049      -0.112925
 C         0.157054      -0.162307       1.278746
 C         1.298781       0.038934      -0.952916
 C        -2.003701      -0.367854       2.596176
 N         2.427484       0.081014      -0.526540
 N        -0.984234      -0.275731       2.035079
 N        -1.090286      -0.117278      -0.745857
 N         1.332038      -0.128616       1.894892
 H        -1.975056      -0.198822      -0.273958
 H        -1.060064      -0.055618      -1.752483
 H         1.399428      -0.183093       2.894540
 H         2.144025      -0.041716       1.254466
12
15 MIN S1
 C         0.447703      -0.064566      -0.421609
 C        -0.411717       0.047727       0.741393
 C        -0.689427      -0.130881      -1.276290
 C        -0.291508       0.169368       2.117159
 N        -1.143522      -0.234355      -2.476906
 N        -0.151685       0.269897       3.258694
 N         1.774578      -0.089563      -0.571305
 N        -1.505096      -0.014487      -0.067919
 H         2.382413      -0.026840       0.224984
 H         2.190262      -0.177624      -1.480049
 H        -2.496875       0.006992       0.109399
 H        -0.404444      -0.303160      -3.165056
```

S_1 transition states and S_1/S_0 intersections

```
12
4-11 TS S1
 C         0.601818      -0.001408      -0.466664
 C        -0.099115      -0.094320       0.781307
 C        -0.079607      -0.243936      -1.668718
 C         0.232004      -1.384174       1.946784
 N        -0.747591      -0.382276      -2.603470
 N         0.685148      -0.243556       2.010571
 N         1.907270       0.336599      -0.445597
 N        -1.301265       0.544309       0.854795
 H         2.364151       0.411438       0.450109
 H         2.432555       0.492287      -1.288068
 H        -1.695126       0.747342       1.760500
 H        -1.927899       0.520898       0.065516
12
TS 5-7 S1 (TD-CAM-B3LYP/6-31G*)
 C         0.720889       0.031946      -0.388200
 C        -0.387628      -0.044623       0.509082
 C         0.097273       0.101691      -1.689810
 C        -0.390086       0.129127       1.923137
 N        -0.126019      -0.360285      -2.848547
 N        -0.364767       0.248486       3.076415
 N         2.034083       0.033533      -0.143198
 N        -1.432735      -0.103096      -0.315935
 H         2.405013       0.072258       0.794936
 H         2.673125       0.096901      -0.922248
 H        -2.359624       0.095340       0.061687
 H        -1.026639      -0.093397      -3.257270
12
CI 1
 C         0.747789      -0.237712      -0.753781
 C         0.574056      -0.051934       0.681630
 C        -0.306415      -0.973404      -1.314071
 C        -0.421678       0.843571       1.225545
 N        -1.170775      -1.631536      -1.707383
 N        -1.192936       1.604119       1.594617
 N         1.372137       0.789175      -1.517164
 N         1.343729      -0.647942       1.554599
 H         2.356124       0.879234      -1.385606
 H         0.918696       1.680937      -1.504727
 H         1.247514      -0.519647       2.540311
 H         2.029716      -1.286762       1.210876
 12
CI 1 (CASSCF)
 C         0.760277      -0.256253      -0.757687
 C         0.584677      -0.060798       0.671919
 C        -0.306249      -0.979706      -1.307334
 C        -0.415279       0.840982       1.221746
 N        -1.183202      -1.626456      -1.692873
 N        -1.191128       1.604069       1.569148
 N         1.369101       0.795080      -1.502922
 N         1.342078      -0.643871       1.545671
 H         2.350995       0.883447      -1.381395
 H         0.918372       1.684946      -1.473392
 H         1.241908      -0.511253       2.528940
 H         2.026406      -1.282089       1.203026
12
CI 2
 C         0.499329       0.085543      -0.527531
 C        -0.507104       0.090172       0.477951
 C         0.077843      -0.004301      -1.900136
 C        -0.141236       0.139818       1.891861
 N        -0.324811      -0.080877      -2.975429
 N         0.912075       0.196990       2.489042
 N         1.775072       0.146589      -0.209819
 N        -1.813596       0.047074       0.171801
 H         1.934398       0.197946       1.481129
 H         2.444679       0.136661      -0.965425
 H        -2.480281       0.359229       0.864334
 H        -2.123996      -0.043329      -0.784093
12
CI 2 (CASSCF)
 C         0.514033       0.006361      -0.561388
 C        -0.496431       0.049382       0.467555
 C         0.096009      -0.009264      -1.896741
 C        -0.032582       0.044314       1.855473
 N        -0.661318      -0.004646      -2.831324
 N         0.317999       0.057806       2.928324
 N         1.863551      -0.138016      -0.233960
 N        -1.767979       0.111604       0.178051
 H         2.161063       0.371611       0.570572
 H         2.475480       0.013769      -1.004772
 H        -2.325584       0.143098       1.012359
 H        -1.661790       0.025921      -2.723357
12
CI 3 (TD-CAM-B3LYP/6-31G*)
 C         0.754726       0.006157      -0.533845
 C        -0.286871      -0.013309       0.328923
 C        -1.929829       0.248010      -1.452735
 C        -0.211606      -0.310445       1.712097
 N        -1.942454      -0.202625      -2.577576
 N        -0.132358      -0.526446       2.850039
 N         2.054311       0.011684      -0.261439
 N        -1.615403       0.249321      -0.182451
 H         2.422667       0.154625       0.676030
 H         2.726632      -0.184852      -0.985623
 H        -2.192590       0.814860       0.448274
 H        -1.453477      -1.092043      -2.757867
12
CI 3 (CASSCF)
```

```
 C         0.376540      -0.207283      -0.460744
 C        -0.513397       0.204625       0.671352
 C        -0.733560      -0.676922      -1.202576
 C        -0.347349       0.165058       2.076617
 N        -0.818551      -0.118507      -2.495940
 N        -0.155106       0.208022       3.204474
 N         1.652856      -0.037570      -0.670813
 N        -1.556277      -0.150355      -0.073315
 H         2.240429       0.384551       0.009421
 H         2.043636      -0.309365      -1.545479
 H        -2.473778      -0.388449       0.233637
 H        -1.520506       0.603481      -2.508253
12
CI 7-18
 C         0.354524       0.012013      -0.346849
 C        -0.497203      -0.016190       0.779533
 C        -0.899326      -0.009746      -1.233060
 C        -0.244040       0.088570       2.175274
 N        -0.824219      -0.970784      -2.208472
 N         0.030194       0.172658       3.293857
 N         1.638820      -0.074263      -0.633455
 N        -1.658253      -0.170540       0.151242
 H         2.350549      -0.213384       0.067991
 H         1.907516      -0.128292      -1.606337
 H        -1.283279       1.010944      -1.480006
 H        -1.689981      -1.019458      -2.745691
```

4HCN in water cluster

```
39
4 + 9 H2O MIN S0 (B3LYP/6-31G**)
 C         0.328400    -0.032865    -0.013859
 C        -0.856961     0.194271     0.662555
 C         0.397943     0.192416    -1.408724
 C        -0.802505     0.016447     2.099514
 N         0.544289     0.382473    -2.554978
 N        -0.861240    -0.074896     3.256298
 N         1.491315    -0.498709     0.670442
 N        -2.062885     0.544585     0.182567
 H         1.653327    -1.506837     0.519730
 H         2.324297     0.012685     0.344743
 H        -2.848992     0.706260     0.828876
 H        -2.253824     0.631191    -0.828377
 O        -3.023398     0.841926    -2.457380
 H        -3.170039     1.780594    -2.645744
 H        -2.536650     0.509531    -3.251484
 O         3.754891     0.997764    -0.495463
 H         3.974847     1.799412     0.000881
 H         3.554955     1.321200    -1.405499
 O         2.224394    -3.331808     0.919545
 H         2.357651    -2.972248     1.833965
 H         3.128031    -3.425109     0.581508
 O        -4.226604     0.969462     1.972305
 H        -4.882405     0.262774     1.879316
 H        -3.986926     0.961564     2.930150
 O        -1.463264     0.021376    -4.578096
 H        -1.536275    -0.939594    -4.684717
 H        -0.623739     0.147246    -4.088297
 O         3.040279     1.849420    -3.051153
 H         3.504264     1.277407    -3.681707
 H         2.121810     1.511781    -3.054555
 O        -3.344311     0.843248     4.590089
 H        -3.141202     1.736545     4.907661
 H        -2.472520     0.445850     4.404044
 O         2.518976    -1.774142     3.143236
 H         2.103623    -1.077147     2.596246
 H         1.870157    -1.942431     3.862149
 O         0.602200    -1.809528     5.209018
 H         1.041718    -1.168486     5.788719
 H        -0.053672    -1.279327     4.719844
```

Final Tautomerization (water)

```
15
17 + 1 H2O MIN S0 (+PCM)
 C        -0.42742       1.02687      -0.02014
 C        -0.95192      -0.23823       0.00980
 C         1.31817      -0.45510      -0.00893
 N         0.93065       0.85468      -0.02950
 H         1.59000       1.61454      -0.05551
 N         0.15766      -1.10226       0.01274
 H         0.08335      -2.10477       0.03050
 N        -1.01981       2.24079      -0.09762
 H        -1.99917       2.28829       0.12781
 H        -0.48813       3.03689       0.21284
 C        -2.29076      -0.63912       0.03513
 N        -3.39688      -0.95460       0.05574
 H         3.21826      -0.81757      -0.03461
 O         4.20284      -0.88017      -0.02838
 H         4.44244      -0.78784       0.89721
15
17-2 + 1 H2O TS S0 (+PCM)
 C        -0.26215       0.86922      -0.01005
 C        -0.95772      -0.32162      -0.00255
 C         1.20719      -0.81247      -0.02413
 N         1.05710       0.51600      -0.02205
 H         1.92133       1.05705      -0.02467
 N         0.00621      -1.33973      -0.01399
 H        -0.19323      -2.32683      -0.01603
 N        -0.69083       2.14229      -0.05481
 H        -1.65844       2.32484       0.14832
 H        -0.05082       2.87444       0.20128
 C        -2.33987      -0.54086       0.01525
 N        -3.47764      -0.70256       0.02914
 H         2.32534      -1.08256      -0.02735
 O         3.68206      -0.25840      -0.06756
 H         4.05082      -0.25737       0.81974
15
2 + 1 H2O MIN S0 (+PCM)
 C        -0.17236       0.69651      -0.00806
 C        -1.03507      -0.38554       0.00870
 C         1.04306      -1.07003      -0.02047
 N         1.11066       0.24753      -0.02523
 H         2.94304       0.73560      -0.04748
 N        -0.21072      -1.50638      -0.00095
 H        -0.50808      -2.46784       0.00844
 N        -0.46332       2.02601      -0.06215
 H        -1.37178       2.31120       0.26313
 H         0.28252       2.63795       0.22495
 C        -2.43271      -0.43129       0.02501
 N        -3.58328      -0.44317       0.03762
 H         1.89341      -1.73007      -0.02975
 O         3.91827       0.72229      -0.05921
 H         4.16932       0.53276       0.84818
15
17-19 + 1 H2O TS S0 (+PCM)
 C        -0.85463600   -0.95471800    0.00545300
 C        -0.60375900    0.40046100   -0.00379300
 C         1.35561900   -0.64271000   -0.02008600
 N         0.37635300   -1.56405200   -0.00623100
 H         0.53111500   -2.55961300   -0.00198400
 N         0.78265600    0.52978100   -0.01546600
 H         1.40854600    1.33414300   -0.02271800
 N        -2.00949200   -1.64084500    0.07425500
 H        -2.86445700   -1.14074600   -0.10104700
 H        -2.01562600   -2.60686500   -0.20680000
 C        -1.51208000    1.46630800   -0.00191700
 N        -2.27292600    2.32722700   -0.00061600
 H         2.49650700   -0.54786800   -0.03392200
 O         3.51838900    0.69102500   -0.08545000
 H         3.84980600    0.81192500    0.80853100
15
19 + 1 H2O MIN S0 (+PCM)
 C        -0.95966700   -1.09925000    0.02371800
 C        -0.48654600    0.19862300    0.00165100
 C         1.24546400   -1.05451100   -0.03088800
 N         0.15419100   -1.87586300    0.00315000
 H         0.17361000   -2.88234800    0.02384400
 N         0.90095100    0.19199500   -0.03008700
 H         2.41083900    1.32461800   -0.05289100
 N        -2.21852300   -1.60242300    0.12116600
 H        -2.96462900   -0.95767600   -0.08192100
 H        -2.37395000   -2.52054300   -0.26268900
 C        -1.25566800    1.37597200    0.00595300
 N        -1.90329100    2.32621500    0.00953700
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 H         2.25215800   -1.43343600   -0.05698300
 O         3.30148800    1.72554200   -0.05821500
 H         3.61823900    1.62407500    0.84267800
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Final Tautomerization (dimer)

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24
17:17 MIN S0 (cc-pVTZ)
 C        -3.55969  -0.33331   0.00773
 C        -2.80841   0.80685   0.01835
 C        -1.36530  -0.95812   0.03997
 N        -2.62825  -1.38469   0.02661
 H        -2.88490  -2.35490   0.02582
 N        -1.50465   0.40028   0.03748
 H        -0.66925   1.00228   0.05083
 C         1.37490   0.97809   0.01435
 N         1.50161  -0.38154   0.01279
 H         0.66051  -0.97681   0.01256
 N         2.64243   1.39232  -0.00604
 H         2.90859   2.35995  -0.01198
 C         2.80094  -0.80076  -0.00498
 C         3.56373   0.33161  -0.01415
 C         4.95860   0.46277  -0.01897
 N         6.10514   0.54901  -0.01975
 N         3.15694  -2.11667  -0.06833
 H         4.12469  -2.32004   0.11671
 H         2.51698  -2.77256   0.34627
 N        -3.17973   2.11891   0.06974
 H        -2.53580   2.78144  -0.32787
 H        -4.14425   2.31184  -0.14141
 C        -4.95226  -0.48227  -0.03164
 N        -6.09662  -0.58745  -0.06860
24
17:17-2:2 TS S0 (cc-pVTZ)
 C        -3.40538  -0.32459  -0.00436
 C        -2.74107   0.87496   0.01894
 C        -1.20034  -0.75211   0.01954
 N        -2.40406  -1.30679   0.00088
 H        -2.57930  -2.29574  -0.01322
 N        -1.41062   0.57896   0.03225
 H        -0.50720   1.16825   0.04907
 C         1.28142   0.93819   0.04118
 N         1.36210  -0.42373   0.04496
 H         0.14089  -0.95366   0.03057
 N         2.54829   1.36653  -0.00078
 H         2.82062   2.33198  -0.01735
 C         2.66048  -0.82344   0.00561
 C         3.45108   0.29600  -0.02030
 C         4.84599   0.40991  -0.03994
 N         5.99470   0.48025  -0.05143
 N         3.02681  -2.14566  -0.05624
 H         3.99369  -2.33433   0.15043
 H         2.39556  -2.78048   0.40229
 N        -3.21843   2.14534   0.08009
 H        -2.60922   2.87949  -0.23579
 H        -4.19097   2.27817  -0.13705
 C        -4.78264  -0.58167  -0.03744
 N        -5.91612  -0.76876  -0.06806
24
2:2 MIN S0 (cc-pVTZ)
 C        -3.67654  -0.32428  -0.00535
 C        -2.96747   0.85898   0.01587
 C        -1.51485  -0.70954  -0.00010
 N        -2.70322  -1.31921  -0.01276
 H        -2.87329  -2.30852  -0.02792
 N        -1.63472   0.60117   0.01657
 H         0.64288   1.38765   0.09959
 C         1.55861   0.81936   0.06852
 N         1.60664  -0.49568   0.07557
 H        -0.56838  -1.22552  -0.00228
 N         2.77869   1.36181   0.01323
 H         3.00356   2.34019  -0.00308
 C         2.92076  -0.82830   0.02070
 C         3.69387   0.31311  -0.01678
 C         5.08569   0.46370  -0.05667
 N         6.23205   0.54739  -0.08287
 N         3.31889  -2.13422  -0.03881
 H         4.27256  -2.33111   0.21114
 H         2.64888  -2.79381   0.31690
 N        -3.44127   2.13933   0.08175
 H        -2.78986   2.84279  -0.22003
 H        -4.38895   2.29053  -0.21835
 C        -5.05584  -0.56546  -0.03193
 N        -6.19202  -0.73937  -0.05959
24
17:17-2:19 TS S0 (cc-pVTZ)
 C         3.43783  -0.78364   0.01854
 C         2.88915   0.46640  -0.01138
 C         1.19495  -0.98632  -0.02038
 N         2.37741  -1.65482   0.01319
 H         2.46070  -2.65575  -0.01230
 N         1.51036   0.29325  -0.04318
 H         0.65879   0.96020  -0.06371
 N         4.74211  -1.20405  -0.02126
 H         5.41668  -0.45534   0.00110
 H         4.98340  -1.94791   0.61466
 C         3.56898   1.69849   0.00193
 N         4.17342   2.67402   0.01731
 C        -1.13486   0.85968  -0.06058
 N        -1.33607  -0.49006  -0.05778
 H        -0.14992  -1.10626  -0.03488
 N        -2.35762   1.40001  -0.01231
 H        -2.54004   2.38656   0.00417
 C        -2.66426  -0.77120  -0.00772
 C        -3.35189   0.41426   0.01823
 C        -4.73157   0.64852   0.04452
 N        -5.87038   0.81449   0.06155
 N        -3.14808  -2.05634   0.06255
 H        -4.13095  -2.15313  -0.13310
 H        -2.58676  -2.74094  -0.41530
24
2:19 MIN S0 (cc-pVTZ)
 C         3.75179  -0.82900   0.02778
 C         3.11978   0.38829  -0.00735
 C         1.55734  -1.06441  -0.01233
 N         2.74551  -1.74657   0.02593
 H         2.86446  -2.74298  -0.02167
 N         1.75014   0.21509  -0.03935
 H        -0.42989   1.19466  -0.10731
 N         5.08328  -1.18731  -0.01067
 H         5.70082  -0.39105  -0.05382
 H         5.37244  -1.82620   0.71480
 C         3.75247   1.65238  -0.00208
 N         4.30743   2.65701   0.00821
 C        -1.39562   0.71566  -0.07574
 N        -1.57020  -0.58921  -0.08695
 H         0.59141  -1.54200  -0.01190
 N        -2.55756   1.37306  -0.01299
 H        -2.68426   2.36889   0.01034
 C        -2.91001  -0.79239  -0.02657
 C        -3.56973   0.41779   0.01829
 C        -4.94135   0.69747   0.06539
 N        -6.07566   0.88314   0.09759
 N        -3.43447  -2.05446   0.03119
 H        -4.40310  -2.15313  -0.22014
 H        -2.83461  -2.77152  -0.33829
24
17:17-19:19 TS S0 (cc-pVTZ)
 C         3.28703   0.92526   0.00165
 C         2.86602  -0.37414   0.00968
 C         1.03641   0.90401   0.00517
 N         2.14533   1.68677  -0.00220
 H         2.12408   2.69084   0.03557
 N         1.47576  -0.33787   0.02003
 H         0.70525  -1.08395   0.02583
 N         4.54164   1.47168   0.06725
 H         5.28975   0.79726   0.03256
 H         4.71178   2.25946  -0.53770
 C         3.66403  -1.53256  -0.00446
 N         4.36044  -2.44488  -0.01947
 C        -1.13321  -1.12696   0.01266
 N        -1.42916   0.17102  -0.00100
 H        -0.29538   0.90222  -0.00191
 N        -2.35157  -1.77033   0.00235
 H        -2.45619  -2.76771  -0.04591
 C        -2.81152   0.34764  -0.00736
 C        -3.39222  -0.88717  -0.01166
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 C        -3.46913   1.59234   0.00391
 N        -4.03214   2.59465   0.01648
 N        -4.71359  -1.28507  -0.09313
 H        -4.98259  -1.98068   0.58637
 H        -5.35824  -0.50962  -0.08435
24
19:19 MIN S0 (cc-pVTZ)
 C         3.57427   0.96084   0.00235
 C         3.06469  -0.31324   0.00834
 C         1.36681   0.97839   0.01159
 N         2.48282   1.77444   0.00287
 H         2.49996   2.77691   0.06785
 N         1.68359  -0.27651   0.02139
 H        -0.44213  -1.53418   0.02055
 N         4.86414   1.44658   0.06711
 H         5.55568   0.71317   0.09997
 H         5.09707   2.12737  -0.64027
 C         3.82035  -1.50759  -0.00470
 N         4.47375  -2.45134  -0.01944
 C        -1.42481  -1.09165   0.00389
 N        -1.66633   0.17932  -0.00428
 H         0.35925   1.36037   0.00287
 N        -2.58785  -1.81819  -0.00109
 H        -2.66633  -2.81752  -0.07016
 C        -3.04144   0.30141  -0.00472
 C        -3.62806  -0.93892  -0.00840
 C        -3.71146   1.54591   0.00375
 N        -4.28490   2.54024   0.01386
 N        -4.94435  -1.34374  -0.08861
 H        -5.22643  -2.01456   0.61028
 H        -5.58979  -0.56968  -0.12453
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