

Supporting Information

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

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Table of Contents

COMPUTATIONAL DETAILS	1
PREDOMINANCE OF TRANS IN THE PHOTOSTATIONARY STATE	1
THERMODYNAMIC AND SPECTROSCOPIC DATA	1
CASPT2 DATA	4
FINAL TAUTOMERIZATION	4
REACTION PATHS	5
REFERENCES	5
CARTESIAN COORDINATES.....	6
<i>S</i> ₀ minima	6
<i>S</i> ₀ Transition states.....	7
Triplet structures	9
<i>S</i> ₁ minima	9
<i>S</i> ₁ transition states and <i>S</i> ₁ / <i>S</i> ₀ intersections	10
4HCN in water cluster.....	11
Final Tautomerization (water)	11
Final Tautomerization (dimer).....	12

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 Å³ 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.

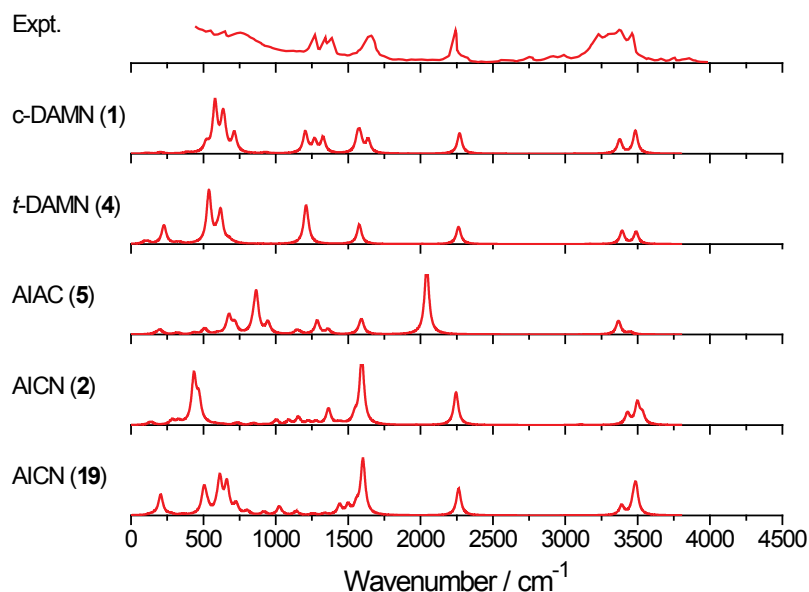


Figure 1. IR spectra of the main isomers of the HCN tetramer computed at the CAM-B3LYP/aug-cc-pVTZ level. Computational wavenumbers multiplied by 0.95 to account for anharmonic effects. Experimental spectrum (Fourier Transform Infrared Photoacoustic Spectroscopy) for *cis*-DAMN isomer from Ref.^[22]. 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.

Assignment	CC2 aug-cc-pVDZ		TD-B3LYP aug-cc-pVDZ		TD-CAM-B3LYP aug-cc-pVDZ		TD-CAM-B3LYP aug-cc-pVTZ	
	ΔE (eV)	f	ΔE (eV)	f	ΔE (eV)	f	ΔE (eV)	f
<i>cis</i> -DAMN (1)								
CS	0.00	-	0.00	-	0.00	-	0.00	-
$\pi_{\text{CC}}\text{-Ryd}(3s_+(\text{NH}_2))$	4.73	0.021	4.37	0.063	4.79	0.013	4.82	0.015
$\pi_{\text{CC}}\text{-}\pi_{\text{CC}}^*$	4.91	0.416	4.45	0.285	4.63	0.374	4.71	0.373
$\pi_{\text{CC}}\text{-Ryd}(3s_-(\text{NH}_2))$	5.69	0.001	5.37	0.002	5.84	0.002	5.86	0.002
$\pi_{\text{CC}}\text{-}\sigma_{\text{CN}}^*$	5.84	0.006	5.22	0.013	5.63	0.011	5.68	0.010
<i>trans</i> -DAMN (4)								
CS	[+0.03]		[+0.02]		[+0.02]		[+0.02]	
CS	0.00	-	0.00	-	0.00	-	0.00	-
$\pi_{\text{CC}}\text{-}\pi_{\text{CC}}^*$	4.37	0.307	3.93	0.247	4.15	0.286	4.21	0.281
$\pi_{\text{CC}}\text{-}\sigma_{\text{CN}}^*$	5.13	0.001	4.45	0.002	4.92	0.002	4.96	0.001
$\pi_{\text{CC}}\text{-Ryd}(3s_+(\text{NH}_2))$	5.00	0.015	4.75	0.012	5.14	0.013	5.13	0.014
$\pi_{\text{CC}}\text{-}\sigma_{\text{CN}}^*$	5.89	0.002	5.41	0.003	5.87	0.002	5.88	0.002
AICN (2)								
CS	[-0.86]		[-0.93]		[-1.06]		[-1.05]	
CS	0.00	-	0.00	-	0.00	-	0.00	-
$\pi_{\text{CC}}\text{-Ryd}(3s(\text{NH}))$	5.08	0.010	4.72	0.002	5.13	0.008	5.14	0.010
$\pi_{\text{CC}}\text{-}\pi_{\text{CC}}^*$	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	<i>cis</i> -DAMN	<i>trans</i> -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	<i>G</i> / 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.

Isomer	Optim.	S ₀ / au	Relative energy / eV					Absolute energy / eV				
			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 S₁ and S₀ 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.

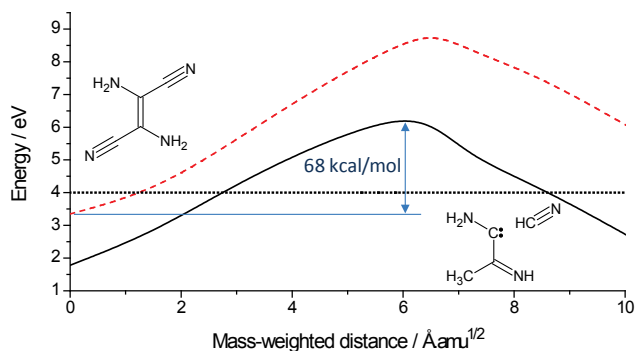


Figure 2. Energy profile for the ground and first excited state along the LIIC pathway between the S_1 minimum of *trans*-DAMN (**4**) and the ground-state minimum of **14**.

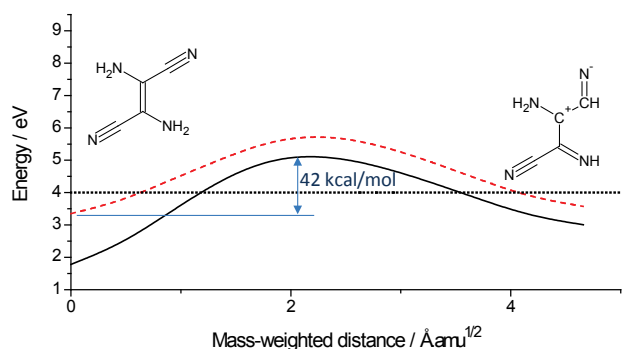


Figure 3. Energy profile for the ground and first excited state along the LIIC pathway between the S_1 minimum of **4** and the ground-state minimum of **10**.

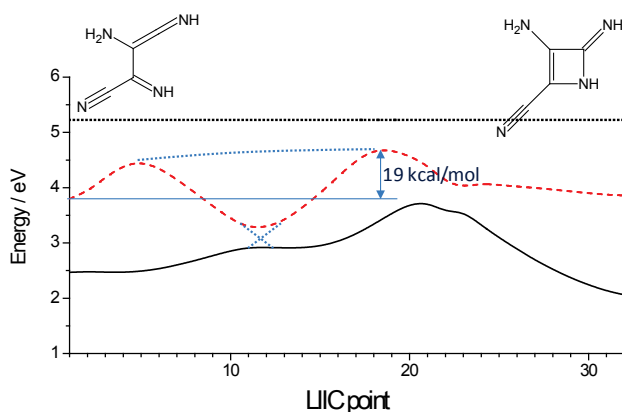


Figure 4. Energy profile for the ground and first excited state along the LIIC pathway between the twisted S_1 minimum of **5** and the S_1 minimum of **7**. The crossing lines around LIIC point 11

indicate a state crossing at the planar geometry. The dotted line connecting the two maxima illustrates an alternative path not involving the crossing.

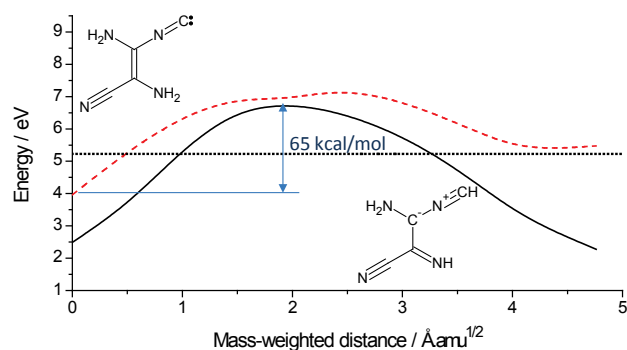


Figure 5. Energy profile for the ground and first excited state along the LIIC pathway between the S_1 minimum of **11** and the ground-state minimum of **12**.

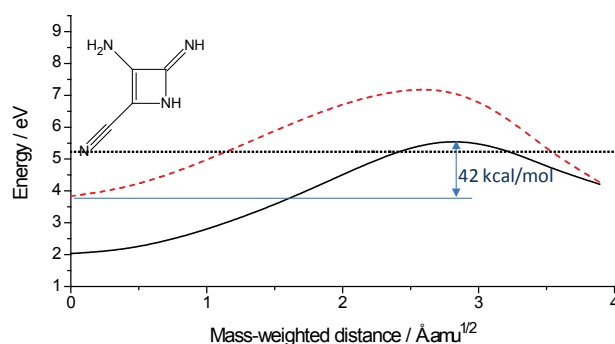


Figure 6. Energy profile for the ground and first excited state along the LIIC pathway between the S_1 minimum of **7** and the S_1/S_0 intersection that leads to **18**.

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Cartesian coordinates

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

S₀ minima

12
1 MIN SO
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 SO
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 SO
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 SO
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

7 MIN SO				H	2.386973	0.035783	0.169354
C	0.395480	-0.046549	-0.331749	H	2.091303	0.092732	-1.501856
C	-0.426679	-0.009231	0.736021	H	-2.332304	0.525021	-0.053534
C	-0.803985	-0.178361	-1.200594	H	-0.286839	-0.088720	-3.062894
C	-0.273748	0.052658	2.127728	12			
N	-0.969587	-0.212924	-2.434887	17 MIN SO			
N	-0.133851	0.125462	3.265817	C	0.587212	-0.017244	-0.376887
N	1.705215	-0.092742	-0.616329	C	-0.347599	0.229170	0.579532
N	-1.666611	-0.235639	-0.040057	C	-1.474232	-0.075890	-1.396828
H	2.391281	0.085644	0.093934	C	-0.164825	0.458560	1.950746
H	1.988143	0.002136	-1.574809	N	-0.116089	-0.196167	-1.540979
H	-2.338795	0.524645	-0.000635	N	0.007028	0.641542	3.072202
H	-1.948653	-0.304719	-2.695890	N	1.954840	-0.032557	-0.317634
12				N	-1.581935	0.188399	-0.091556
10 MIN SO				H	2.344225	0.017823	0.609728
C	0.445453	0.075414	-0.471051	H	2.419257	-0.710085	-0.899579
C	-0.565084	-0.023128	0.582424	H	-2.465284	0.344117	0.358785
C	0.116189	0.418554	-1.902720	H	0.309203	-0.362057	-2.435312
C	-0.152152	0.358956	1.916309	12			
N	1.063747	0.452112	-2.702767	18 MIN SO			
N	0.192203	0.619845	2.975433	C	0.906389	0.843595	-0.070030
N	1.689177	-0.164214	-0.264682	C	-0.262514	0.150911	0.430605
N	-1.739973	-0.389211	0.271972	C	-1.308324	0.098762	-1.608489
H	2.101096	-0.395877	0.624694	C	-0.258508	-0.059210	1.863663
H	2.222558	0.007126	-1.144536	N	-1.876189	-0.603781	-2.484674
H	-2.371089	-0.386268	1.070389	N	-0.176374	-0.238232	2.991007
H	-0.960005	0.559013	-2.079853	N	1.964756	0.153438	-0.316238
12				N	-1.294655	-0.193769	-0.239263
11 MIN SO				H	2.044353	-0.853958	-0.194567
C	0.162334	-0.080216	1.297712	H	2.796356	0.613795	-0.658631
C	0.114140	-0.046346	-0.048340	H	-0.813844	1.028452	-1.902814
C	-2.025150	-0.309231	2.570388	H	-2.299864	-1.428413	-2.059789
C	1.348561	0.013911	-0.753763	12			
N	-1.018867	-0.192448	1.995318	19 MIN SO			
N	2.361033	0.036012	-1.292758	C	0.522724	-0.042711	-0.359899
N	1.288847	0.081636	2.084659	C	-0.397335	0.095181	0.649387
N	-1.056818	0.036906	-0.805128	C	-1.539445	-0.225363	-1.116562
H	2.163694	0.069278	1.584068	C	-0.082120	0.315470	2.010570
H	1.304172	-0.479277	2.921556	N	-0.216169	-0.248103	-1.484442
H	-1.024840	-0.467377	-1.676707	N	0.250426	0.489383	3.095013
H	-1.899366	-0.158979	-0.287795	N	1.895999	0.066660	-0.378047
12				N	-1.679672	-0.017538	0.149890
12 MIN SO				H	2.292028	0.245029	0.532166
C	0.424848	0.138038	-0.524142	H	2.384980	-0.678006	-0.850446
C	-0.585579	0.114527	0.531319	H	-2.333769	-0.375971	-1.827325
C	-0.367407	0.802938	-2.772947	H	0.145953	-0.320852	-2.418614
C	-0.072137	-0.024738	1.883681				
N	0.033391	0.368404	-1.712586	S₀ Transition states			
N	0.332887	-0.127247	2.949540	12			
N	1.763854	-0.159576	-0.247895	4-5 TS SO			
N	-1.827024	0.224809	0.284232	C	0.641231	0.160935	-0.682194
H	2.027171	-0.048579	0.718756	C	-0.461075	0.228866	0.249126
H	2.418488	0.293097	-0.866695	C	0.025529	0.041099	-1.891494
H	-2.387640	0.219824	1.130149	C	-0.075925	0.258227	1.642538
H	-0.732322	0.095072	-3.521572	N	-0.985090	0.018072	-2.504754
12				N	0.212285	0.285355	2.749875
14 MIN SO				N	1.990727	-0.059136	-0.370860
C	-0.865607	0.199390	-0.090126	N	-1.712237	0.169876	-0.087876
C	0.309561	0.080941	-0.938665	H	2.177480	-0.898171	0.156343
C	1.811097	-0.202760	2.679354	H	2.453676	0.731372	0.049067
C	0.042251	0.052810	-2.363920	H	-2.351907	0.149265	0.694254
N	1.676955	-0.506315	3.771981	H	-1.730243	-0.272620	-1.732714
N	-0.141658	-0.018340	-3.491146	12			
N	-1.053037	-0.764490	0.741546	4-10 TS SO			
N	1.489804	0.119029	-0.455300	C	0.484626	0.092740	-0.387488
H	-0.452789	-1.584954	0.811735	C	-0.497030	-0.039701	0.610972
H	-1.802628	-0.714364	1.416883	C	-0.178375	0.259657	-1.743627
H	2.201899	0.181986	-1.177101	C	-0.144667	0.375697	1.939177
H	1.895701	0.053888	1.634430	N	0.226330	0.497146	-2.841771
12				N	0.141910	0.668255	3.009242
15 MIN SO				N	1.783766	-0.113396	-0.281720
C	0.423813	-0.050216	-0.354413	N	-1.705905	-0.406156	0.262547
C	-0.414386	-0.004161	0.696427	H	2.194453	-0.651715	0.461446
C	-0.781615	-0.151046	-1.243398	H	2.392500	0.248873	-1.001023
C	-0.269431	0.053230	2.091060	H	-2.404028	-0.112737	0.943001
N	-1.094539	-0.140064	-2.449713	H	-1.267659	-0.027083	-1.375296
N	-0.128349	0.124417	3.228673	12			
N	1.751050	-0.146503	-0.587775				
N	-1.638786	-0.214721	-0.091061				

4-11 TS S0				H	2.304197	-0.126219	0.064761
C	0.159380	-0.027910	1.339867	H	1.818377	0.290979	-1.544843
C	0.067561	0.018790	-0.007135	H	-1.606789	1.069573	-0.771812
C	-1.199022	0.127079	2.202650	H	-1.932673	-0.677712	-2.626509
C	1.255924	0.281378	-0.760409	12			
N	-1.289624	-1.029870	1.966060	8-2 TS S0			
N	2.173636	0.484342	-1.414953	C	0.611085	0.476560	0.060157
N	1.335303	-0.036369	2.038563	C	-0.417287	-0.559819	0.163160
N	-1.090536	-0.087271	-0.729193	C	2.206757	-0.770499	-0.133182
H	1.861784	-0.895096	2.044899	C	-1.737078	-0.065840	-0.182737
H	1.309956	0.417870	2.936169	N	1.819014	0.342167	-0.608419
H	-1.010848	-0.170499	-1.725996	N	-2.791071	0.316935	-0.419163
H	-1.855744	-0.578586	-0.301293	N	0.319809	1.717748	0.447285
12				N	-0.223311	-1.788315	0.449126
4-14 TS S0				H	-0.518388	1.944885	0.951102
C	0.512696	-0.001512	-0.687613	H	0.936375	2.457246	0.151789
C	-0.475634	0.239540	0.278475	H	-1.060226	-2.335906	0.243096
C	0.172508	0.415919	-2.023442	H	3.290431	-0.907762	-0.040095
C	0.442510	0.301255	1.832502	12			
N	-0.091339	0.696168	-3.101917	8-12 TS S0			
N	0.066863	0.494439	2.917774	C	0.486081	-0.591214	-0.396653
N	1.705200	-0.410568	-0.353070	C	-0.229289	0.276526	0.539661
N	-1.709902	-0.177373	0.296110	C	0.387619	0.643708	-2.010576
H	1.365138	-0.023092	1.180341	C	-0.794081	-0.459290	1.655288
H	2.408996	-0.198855	-1.053924	N	0.310469	-0.601786	-1.772784
H	-2.368614	0.249704	0.931548	N	-1.216988	-1.019950	2.560894
H	-2.031573	-0.994586	-0.202672	N	1.217160	-1.596921	0.082256
12				N	-0.426059	1.530316	0.404749
5-7 TS S0				H	1.427724	-1.695755	1.058926
C	0.594307	-0.109556	-0.392565	H	1.500042	-2.318005	-0.561429
C	-0.370875	-0.051057	0.594494	H	-1.127732	1.852231	1.073163
C	-0.282001	-0.191882	-1.492572	H	0.801023	0.927710	-2.985383
C	-0.187675	0.375050	1.948101	12			
N	-0.552858	-0.001847	-2.653569	10-8 TS S0			
N	-0.032430	0.715595	3.030776	C	0.482149	0.207922	-0.509900
N	1.972388	-0.277159	-0.406100	C	-0.534607	0.007751	0.522931
N	-1.535549	-0.403132	0.037035	C	0.024055	0.363655	-1.917016
H	2.362528	-0.683136	0.427944	C	-0.112860	0.216853	1.894681
H	2.507127	0.514732	-0.726524	N	0.705992	-0.305247	-2.701969
H	-2.338201	0.121875	0.381309	N	0.242225	0.343446	2.975842
H	-1.397641	-0.376713	-3.061189	N	1.757249	0.122132	-0.198077
12				N	-1.727298	-0.285346	0.191511
5-15 TS S0				H	2.080536	-0.290205	0.661169
C	0.631281	-0.086585	-0.405835	H	2.410556	0.211564	-0.965051
C	-0.354477	-0.032159	0.570195	H	-2.348762	-0.334928	0.994981
C	-0.219891	-0.211713	-1.523063	H	-0.937126	0.874733	-2.073482
C	-0.204459	0.410517	1.924282	12			
N	-0.589519	-0.203584	-2.667570	10-14 TS S0			
N	-0.074158	0.761960	3.006375	C	0.147202	-0.181597	-0.663381
N	2.018508	-0.223136	-0.413456	C	-0.728066	-0.156997	0.502329
N	-1.490429	-0.397324	-0.009083	C	0.075466	0.561988	-2.394192
H	2.395041	-0.851650	0.277524	C	-0.127803	0.172982	1.752978
H	2.541745	0.637201	-0.452459	N	1.054586	0.274476	-3.002727
H	-2.329723	0.073613	0.320649	N	0.364266	0.581253	2.739529
H	-0.073148	0.250190	-3.408558	N	1.233488	-0.820668	-0.723221
12				N	-1.950528	-0.467673	0.369093
7-15 TS S0				H	1.645896	-1.387333	0.004160
C	0.420875	-0.087357	-0.327383	H	1.670700	-0.643355	-1.702870
C	-0.417658	-0.015303	0.720351	H	-2.458010	-0.425764	1.249088
C	-0.783607	-0.251963	-1.229573	H	-0.858407	1.096448	-2.483217
C	-0.273836	0.104980	2.109852	12			
N	-1.013853	-0.301261	-2.416892	11-12 TS S0			
N	-0.140674	0.228126	3.244466	C	0.104320	0.011790	1.426126
N	1.741543	-0.148350	-0.581368	C	-0.020617	0.054141	0.039111
N	-1.645865	-0.283996	-0.049463	C	-2.180345	-0.193922	1.473828
H	2.401867	0.100316	0.133556	C	1.153110	-0.090130	-0.761144
H	2.039266	-0.019792	-1.532046	N	-1.089861	-0.172948	2.021779
H	-2.343008	0.454460	-0.040052	N	2.111716	-0.190209	-1.382440
H	-1.173620	-0.353901	-3.390637	N	1.260553	0.076697	2.160777
12				N	-1.245614	0.107455	-0.484873
7-18 TS S0				H	2.116769	0.148396	1.637544
C	0.305839	-0.024815	-0.277167	H	1.313857	-0.537018	2.957715
C	-0.507715	-0.218105	0.825893	H	-1.281970	-0.083020	-1.480403
C	-0.976864	0.059231	-1.107804	H	-2.273109	-0.696824	0.407340
C	-0.285043	-0.122558	2.216642	12			
N	-1.013961	-0.350439	-2.337745	12-2 TS S0			
N	-0.051624	-0.067254	3.338703	C	0.457201	0.037733	-0.428446
N	1.571087	0.100016	-0.586946	C	-0.527196	0.058883	0.634924
N	-1.706610	-0.222319	0.135367	C	-1.123671	0.607059	-2.091324

C	-0.031913	0.027632	1.991203
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	-0.148664	-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	1.273579	-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

S₁ 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	N	-0.364767	0.248486	3.076415
C	-0.351481	0.215006	0.588705	N	2.034083	0.033533	-0.143198
C	0.327985	-0.388647	-1.620663	N	-1.432735	-0.103096	-0.315935
C	-0.541235	-1.047024	1.192683	H	2.405013	0.072258	0.794936
N	-0.112085	-0.935553	-2.585735	H	2.673125	0.096901	-0.922248
N	-0.688067	-2.078278	1.692272	H	-2.359624	0.095340	0.061687
N	1.789812	0.963878	-0.323366	H	-1.026639	-0.093397	-3.257270
N	-1.082898	1.307749	0.733635	12			
H	1.904333	1.475810	0.535895	CI 1			
H	2.437335	1.120652	-1.077872	C	0.747789	-0.237712	-0.753781
H	-1.857657	1.136555	1.365743	C	0.574056	-0.051934	0.681630
H	-0.233680	-1.916558	-2.796591	C	-0.306415	-0.973404	-1.314071
12				C	-0.421678	0.843571	1.225545
7 MIN S1				N	-1.170775	-1.631536	-1.707383
C	0.397348	-0.071827	-0.423072	N	-1.192936	1.604119	1.594617
C	-0.435356	-0.025974	0.757552	N	1.372137	0.789175	-1.517164
C	-0.738900	-0.101045	-1.266257	N	1.343729	-0.647942	1.554599
C	-0.291666	0.107026	2.127934	H	2.356124	0.879234	-1.385606
N	-0.989216	-0.192608	-2.523721	H	0.918696	1.604727	-1.504727
N	-0.136965	0.215676	3.267789	H	1.247514	-0.519647	2.540311
N	1.712743	-0.101280	-0.622316	H	2.029716	-1.286762	1.210876
N	-1.557152	-0.085010	-0.023600	12			
H	2.352087	0.021492	0.141943	CI 1 (CASSCF)			
H	2.071159	-0.059624	-1.560191	C	0.760277	-0.256253	-0.757687
H	-2.488230	0.249247	0.184009	C	0.584677	-0.060798	0.671919
H	-1.977639	-0.245707	-2.731526	C	-0.306249	-0.979706	-1.307334
12				C	-0.415279	0.840982	1.221746
11 MIN S1				N	-1.183202	-1.626456	-1.692873
C	0.072283	-0.085049	-0.112925	N	-1.191128	1.604069	1.569148
C	0.157054	-0.162307	1.278746	N	1.369101	0.795080	-1.502922
C	1.298781	0.038934	-0.952916	N	1.342078	-0.643871	1.545671
C	-2.003701	-0.367854	2.596176	H	2.350995	0.883447	-1.381395
N	2.427484	0.081014	-0.526540	H	0.918372	1.684946	-1.473392
N	-0.984234	-0.275731	2.035079	H	1.241908	-0.511253	2.528940
N	-1.090286	-0.117278	-0.745857	H	2.026406	-1.282089	1.203026
N	1.332038	-0.128616	1.894892	12			
H	-1.975056	-0.198822	-0.273958	CI 2			
H	-1.060064	-0.055618	-1.752483	C	0.499329	0.085543	-0.527531
H	1.399428	-0.183093	2.894540	C	-0.507104	0.090172	0.477951
H	2.144025	-0.041716	1.254466	C	0.077843	-0.004301	-1.900136
12				C	-0.141236	0.139818	1.891861
15 MIN S1				N	-0.324811	-0.080877	-2.975429
C	0.447703	-0.064566	-0.421609	N	0.912075	0.196990	2.489042
C	-0.411717	0.047727	0.741393	N	1.775072	0.146589	-0.209819
C	-0.689427	-0.130881	-1.276290	N	-1.813596	0.047074	0.171801
C	-0.291508	0.169368	2.117159	H	1.934398	0.197946	1.481129
N	-1.143522	-0.234355	-2.476906	H	2.444679	0.136661	-0.965425
N	-0.151685	0.269897	3.258694	H	-2.480281	0.359229	0.864334
N	1.774578	-0.089563	-0.571305	H	-2.123996	-0.043329	-0.784093
N	-1.505096	-0.014487	-0.067919	12			
H	2.382413	-0.026840	0.224984	CI 2 (CASSCF)			
H	2.190262	-0.177624	-1.480049	C	0.514033	0.006361	-0.561388
H	-2.496875	0.006992	0.109399	C	-0.496431	0.049382	0.467555
H	-0.404444	-0.303160	-3.165056	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	0.414860	0.448274
				H	-1.453477	-1.092043	-2.757867
				12			
				CI 3 (CASSCF)			
				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

S₁ transition states and S₁/S₀ intersections

12							
4-11 TS S1							
C	0.601818	-0.001408	-0.466664	H	2.475480	0.013769	-1.004772
C	-0.099115	-0.094320	0.781307	H	-2.325584	0.143098	1.012359
C	-0.079607	-0.243936	-1.668718	H	-1.661790	0.025921	-2.723357
C	0.232004	-1.384174	1.946784	12			
N	-0.747591	-0.382276	-2.603470	CI 3 (TD-CAM-B3LYP/6-31G*)			
N	0.685148	-0.243556	2.010571	C	0.754726	0.006157	-0.533845
N	1.907270	0.336599	-0.445597	C	-0.286871	-0.013309	0.328923
N	-1.301265	0.544309	0.854795	C	-1.929829	0.248010	-1.452735
H	2.364151	0.411438	0.450109	C	-0.211606	-0.310445	1.712097
H	2.432555	0.492287	-1.288068	N	-1.942454	-0.202625	-2.577576
H	-1.695126	0.747342	1.760500	N	-0.132358	-0.526446	2.850039
H	-1.927899	0.520898	0.065516	N	2.054311	0.011684	-0.261439
12				N	-1.615403	0.249321	-0.182451
TS 5-7 S1 (TD-CAM-B3LYP/6-31G*)				H	2.422667	0.154625	0.676030
C	0.720889	0.031946	-0.388200	H	2.726632	-0.184852	-0.985623
C	-0.387628	-0.044623	0.509082	H	-2.192590	0.414860	0.448274
C	0.097273	0.101691	-1.689810	H	-1.453477	-1.092043	-2.757867
C	-0.390086	0.129127	1.923137	12			
N	-0.126019	-0.360285	-2.848547	CI 3 (CASSCF)			

C	0.376540	-0.207283	-0.460744	C	-0.95192	-0.23823	0.00980
C	-0.513397	0.204625	0.671352	C	1.31817	-0.45510	-0.00893
C	-0.733560	-0.676922	-1.202576	N	0.93065	0.85468	-0.02950
C	-0.347349	0.165058	2.076617	H	1.59000	1.61454	-0.05551
N	-0.818551	-0.118507	-2.495940	N	0.15766	-1.10226	0.01274
N	-0.155106	0.208022	3.204474	H	0.08335	-2.10477	0.03050
N	1.652856	-0.037570	-0.670813	N	-1.01981	-2.24079	-0.09762
N	-1.556277	-0.150355	-0.073315	H	-1.99917	2.28829	0.12781
H	2.240429	0.384551	0.009421	H	-0.48813	3.03689	0.21284
H	2.043636	-0.309365	-1.545479	C	-2.29076	-0.63912	0.03513
H	-2.473778	-0.388449	0.233637	N	-3.39688	-0.95460	0.05574
H	-1.520506	0.603481	-2.508253	H	3.21826	-0.81757	-0.03461
12				O	4.20284	-0.88017	-0.02838
CI 7-18				H	4.44244	-0.78784	0.89721

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

H	2.25215800	-1.43343600	-0.05698300
O	3.30148800	1.72554200	-0.05821500
H	3.61823900	1.62407500	0.84267800

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

Final Tautomerization (dimer)

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

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

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