Supporting Information

for

Cyclization of an α,β-unsaturated hydrazone catalyzed by a BINOL-phosphoric acid: pericyclic or not?

Berit Heggen, Mahendra Patil, and Walter Thiel

1 Energies

Table 1: Relative energies E and Gibbs free energies G for the optimized gas-phase structures at B3LYP/6-31G* (gs) and relative energies from single-point calculations using PCM/B3LYP-D/6-311+G** at gas-phase geometries (B3LYP/6-31G*) (SP), in kcal/mol.

	E (gs)	G (gs)	E (SP)
protonated hydrazone **A**			
1	0.00	0.00	0.00
TS-*trans*	18.36	19.66	17.19
TS-*cis*	16.36	18.38	13.70
2-*trans*	10.51	13.27	8.04
2-*cis*	13.94	17.26	9.04
unprotonated hydrazone **B**			
1	0.00	0.00	0.00
TS-*trans*	39.65	40.03	34.18
TS-*cis*	38.62	39.81	31.77
2-*trans*	6.63	8.82	3.90
2-*cis*	9.58	11.79	5.33
pentadienyl anion **C**			
1	0.00	0.00	0.00
TS-*cis*	42.72	42.55	34.80
2-*cis*	32.78	34.11	22.43

2 Additional NBO results

Table 2: Orbital character of occupied lone pairs for the ring atoms in the reactant **1**, the transition state (TS) and the product **2** of the protonated hydrazone **A**, the unprotonated hydrazone **B** and the pentadienyl anion **C** from NBO analysis.

	atom	**character of lone pairs**		
		A	**B**	**C**
1	N1/C1	83.6% p, 16.4% s	94.5% p	
	N2/C2	99.9% p	67.6% p, 32.3% s	
	C3	99.9% p		99.9% p
	C4			
	C5			
TS-*trans*	N1/C1	83.0% p, 17.0% s		
	N2/C2	89.2% p, 10.8% s	54.5% p, 45.5% s	
	C3		96.3% p	
	C4			
	C5	98.6% p		
TS-*cis*	N1/C1	82.8% p, 17.2% s		
	N2/C2	95.2% p	53.9% p, 46.1% s	
			99.8% p	
	C3			
	C4			
	C5	91.7% p, 7.7% d		
2-*trans*	N1/C1			
	N2/C2	79.4% p, 20.6% s	50.5% p, 49.5% s	
			99.7% p	
	C3			
	C4			
	C5			
2-*cis*	N1/C1			
	N2/C2	80.7% p, 19.2% s	50.9% p, 49.1% s	
			99.9% p	
	C3			
	C4			99.9% p
	C5			

3 Orbital correlations for protonated hydrazone A

We searched for ring orbitals at the transition states of **A** with one or more orbital disconnections (typical for pseudopericyclic reactions), in order to correlate them with the respective orbitals of the reactant. These orbitals are shown in Figure 1. Moving from the protonated reactant **1-A** to the TS requires only a rotation of the C5 group, since protonation has already induced a rotation of the N1 group. Clockwise and anticlockwise rotation at C5 lead to the *trans* and *cis* configured transition state, respectively. In the clockwise case (Figure 1), the HOMO-1 at TS-*trans* is correlated with the HOMO-5 of the reactant, while in the anticlockwise case, one can identify a correlation between the HOMO-5 at TS-*cis* and the HOMO-4 of the reactant.

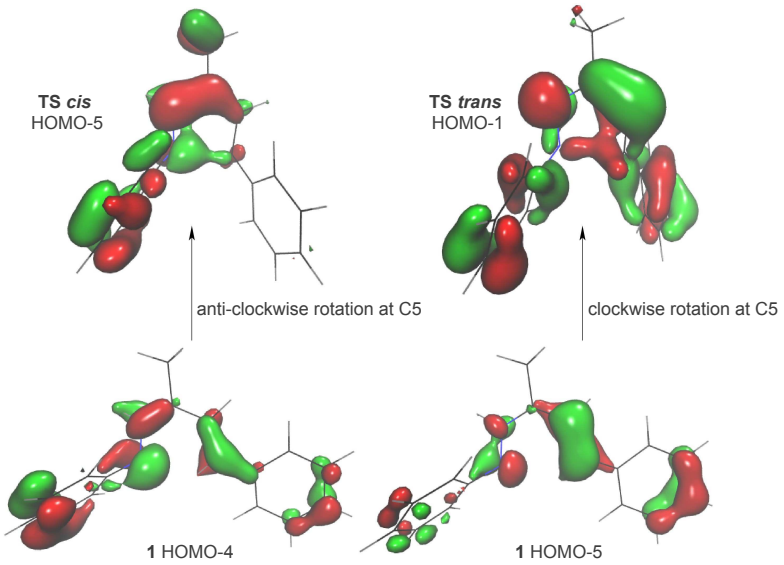

Figure 1: Correlating orbitals at **1-A** and the corresponding transition states that are either *cis* or *trans* configured.

4 Geometrical Data

In this section the coordinates of all minima and transition states are given (in Å) as obtained from gas-phase B3LYP/6-31G* optimizations.

4.1 Protonated hydrazone A

1			
C	-0.172036	2.203397	-0.209302
C	1.118544	1.617054	-0.092302
H	1.882907	2.335789	0.185919
C	1.477726	0.300524	-0.258955
H	0.707422	-0.401269	-0.559779
C	-0.291039	3.688046	0.013955
H	0.231091	4.226313	-0.785912
H	0.186932	3.963862	0.959076
H	-1.328861	4.031357	0.034664
C	-2.680125	-0.327856	-0.279303
C	-3.442779	-1.161323	-1.103620
H	-3.136862	-1.347499	-2.130906
C	-4.599445	-1.752965	-0.598883
H	-5.188778	-2.402896	-1.238364
C	-5.007655	-1.498570	0.712431
H	-5.914280	-1.953906	1.098047
C	-4.244612	-0.659245	1.525725
H	-4.551736	-0.464261	2.548723
C	-3.072846	-0.078051	1.040293
H	-2.460039	0.542597	1.687631
C	2.787700	-0.264926	-0.058194
C	2.948220	-1.650650	-0.295269
H	2.089911	-2.237424	-0.611953
C	4.182831	-2.264245	-0.125719
H	4.292112	-3.328219	-0.310062
C	5.282231	-1.504311	0.283295
H	6.249380	-1.980007	0.416638
C	5.144241	-0.129803	0.524487
H	6.002660	0.453002	0.843422
C	3.913423	0.485965	0.358711
H	3.823397	1.549863	0.553396
N	-1.460137	0.230878	-0.783353
H	-1.360723	0.082444	-1.788003
N	-1.313361	1.593868	-0.507879
H	-2.176319	2.138798	-0.488014

TS-*trans*			
H	1.578787	2.469173	1.434934
H	-4.887776	-2.494594	0.347940
C	-4.039946	-1.846807	0.144771
C	-4.070130	-0.511580	0.570819
C	-2.928973	-2.352892	-0.538920
C	-2.990939	0.321271	0.312774
H	-4.936832	-0.131172	1.102191
C	-1.845830	-1.523554	-0.801411
H	-2.916048	-3.387294	-0.867335
C	-1.864609	-0.171122	-0.387452
H	-3.004171	1.354462	0.647175
H	-0.981453	-1.905365	-1.338159
C	-0.731943	0.669555	-0.688438
H	0.024269	0.194141	-1.312285
C	0.222424	2.803538	-0.078101
C	-0.779870	2.123225	-0.680208
H	-1.630127	2.643867	-1.105720
C	0.393595	4.288335	-0.025377
H	0.448643	4.650048	1.009420
H	1.322564	4.584117	-0.527123
H	-0.437918	4.789886	-0.523475
N	1.183314	2.046432	0.597528
N	0.824193	0.688544	0.751020
H	0.410962	0.510452	1.670648
C	1.820467	-0.297341	0.429390
C	2.777992	-0.057558	-0.560015
C	1.744606	-1.535005	1.076645
C	3.672146	-1.074762	-0.893157
H	2.838192	0.913861	-1.038045
C	2.643977	-2.542368	0.730053
H	0.999411	-1.709617	1.849744
C	3.607963	-2.315567	-0.254543
H	4.426612	-0.891359	-1.651958
H	2.594996	-3.500499	1.238014
H	4.311761	-3.099143	-0.516775

TS-*cis*			
H	1.209741	2.853737	1.640616
H	8.569520	2.484054	-1.845740
C	7.489052	2.484551	-1.734504
C	6.845880	3.615577	-1.216083
C	6.753263	1.354778	-2.110423
C	5.464954	3.621541	-1.072708
H	7.427076	4.485470	-0.926582
C	5.371726	1.356468	-1.970843
H	7.260052	0.483900	-2.513867
C	4.705481	2.494186	-1.460590
H	4.957274	4.492299	-0.669187
H	4.792799	0.486706	-2.271504
C	3.267034	2.480241	-1.338831
H	2.798708	1.605466	-1.788125
C	1.695855	3.887999	-0.145787
C	2.466765	3.707105	-1.238831
H	2.610605	4.500614	-1.963887
C	0.800647	5.050294	0.150716
H	0.871879	5.798450	-0.640866
H	-0.246147	4.728929	0.217310
H	1.066295	5.522391	1.103842
N	1.854284	2.947865	0.864471
N	2.574041	1.805970	0.496316
H	1.964239	1.061586	0.154223
C	3.511385	1.304514	1.462957
C	4.245166	2.188055	2.258969
C	3.708458	-0.077639	1.540848
C	5.174486	1.668548	3.159221
H	4.079934	3.256866	2.181857
C	4.647120	-0.581320	2.438828
H	3.127344	-0.755591	0.918911
C	5.378877	0.289669	3.249904
H	5.741899	2.345551	3.790244
H	4.797805	-1.653791	2.511404
H	6.104179	-0.106329	3.953754

2-*trans*			
N	-0.453389	0.323742	-0.508319
C	-0.311486	4.026834	-0.166392
H	-1.379383	4.279497	-0.184833
H	0.121815	4.358918	-1.116537
H	0.155952	4.585331	0.646989
C	-0.103982	2.560217	0.024747
C	0.546941	1.889633	0.978582
H	1.077702	2.332882	1.810369
C	0.532685	0.406859	0.755633
N	-0.615864	1.700166	-0.997730
H	-1.604603	1.841298	-1.210975
H	0.070044	-0.173077	-1.235853
C	-1.722864	-0.389785	-0.277837
C	-1.994588	-1.520229	-1.044094
C	-2.607280	0.083131	0.693442
C	-3.193562	-2.202317	-0.827387
H	-1.292812	-1.867849	-1.798506
C	-3.801238	-0.607803	0.893913
H	-2.370193	0.962910	1.284981
C	-4.093420	-1.746687	0.136961
H	-3.420780	-3.084861	-1.416513
H	-4.501805	-0.256866	1.644829
H	-5.025108	-2.278915	0.300610
C	1.833271	-0.276271	0.416503
C	2.804856	0.361350	-0.371089
C	2.062766	-1.580706	0.878077
C	3.986206	-0.303792	-0.694779
H	2.643947	1.379669	-0.714753
C	3.248780	-2.240355	0.557594
H	1.319026	-2.075638	1.498533
C	4.209135	-1.603060	-0.230708
H	4.737232	0.194926	-1.299862
H	3.424545	-3.246248	0.926424
H	5.134270	-2.115161	-0.477819
H	0.017602	-0.146280	1.546263

2-*cis*			
N	1.139752	0.026351	-1.077777
C	4.005876	-1.460093	0.754796
H	4.317779	-0.583826	1.337651
H	4.772962	-1.638268	-0.007609
H	3.974334	-2.322797	1.423109
C	2.672354	-1.248394	0.117581
C	1.539641	-1.951109	0.210672
H	1.405622	-2.852705	0.792495
C	0.472794	-1.434157	-0.703475
H	0.510728	-1.926446	-1.683365
C	-0.943738	-1.351052	-0.234267
C	-1.257205	-1.229175	1.127674
H	-0.459939	-1.185196	1.863992
C	-2.587661	-1.184450	1.538820
H	-2.824085	-1.100691	2.595219
C	-3.614918	-1.257290	0.594555
H	-4.651192	-1.228266	0.918023
C	-3.312190	-1.382004	-0.763404
H	-4.109489	-1.453786	-1.496757
C	-1.982066	-1.432811	-1.174880
H	-1.749562	-1.556462	-2.230821
N	2.562061	-0.162025	-0.803126
H	2.949270	0.721063	-0.468459
H	1.054835	0.118774	-2.092027
C	0.551256	1.235898	-0.473036
C	-0.217033	2.061080	-1.290856
C	0.775965	1.530040	0.872055
C	-0.776292	3.217323	-0.745733
H	-0.378212	1.817673	-2.338566
C	0.214270	2.691667	1.400951
H	1.364278	0.868202	1.499052
C	-0.559237	3.532482	0.596438
H	-1.371825	3.871638	-1.374035
H	0.381156	2.937181	2.444877
H	-0.990236	4.435908	1.016205

4.2 Unprotonated hydrazone B

1			
H	-6.388574	1.836991	-0.238724
C	-5.408086	1.381785	-0.129675
C	-5.036726	0.307291	-0.943859
C	-4.506621	1.869775	0.817290
C	-3.780920	-0.276726	-0.810770
H	-5.728340	-0.072061	-1.691506
C	-3.248761	1.285351	0.949692
H	-4.781757	2.707179	1.452902
C	-2.862701	0.195570	0.147228
H	-3.504479	-1.096939	-1.467064
H	-2.551505	1.668815	1.691261
C	-1.530002	-0.386253	0.341398
H	-0.880217	0.184383	1.003080
C	0.225079	-2.194378	0.065162
C	-1.086685	-1.568494	-0.147029
H	-1.784954	-2.187847	-0.710882
C	0.243366	-3.704047	0.131750
H	-0.166879	-4.145567	-0.786885
H	1.268587	-4.057820	0.260760
H	-0.366928	-4.075627	0.965294
N	1.379948	-1.611485	0.172483
N	1.485169	-0.266911	0.082305
C	2.751204	0.323594	-0.026868
C	3.926722	-0.386557	0.260095
C	2.832417	1.676826	-0.392035
C	5.158238	0.259263	0.178061
H	3.855950	-1.430911	0.538744
C	4.071453	2.308217	-0.467679
H	1.922940	2.230518	-0.617458
C	5.244583	1.606015	-0.183655
H	6.062922	-0.301056	0.400792
H	4.117056	3.355747	-0.754335
H	6.209984	2.099939	-0.244072
H	0.705020	0.249637	-0.320063

TS-*trans*			
H	-5.140469	-2.054770	0.404033
C	-4.217498	-1.525727	0.181560
C	-4.068938	-0.187492	0.557374
C	-3.176038	-2.182451	-0.478656
C	-2.885274	0.491151	0.276019
H	-4.877164	0.324877	1.072770
C	-1.992536	-1.502297	-0.760664
H	-3.288846	-3.221721	-0.776087
C	-1.832859	-0.154918	-0.394398
H	-2.757345	1.530069	0.567253
H	-1.181793	-2.010627	-1.278001
C	-0.555973	0.552903	-0.679968
H	0.106415	-0.073693	-1.286631
C	0.401540	2.637754	-0.049690
C	-0.516460	1.991953	-0.868771
H	-1.344342	2.524702	-1.321258
C	0.637572	4.123694	-0.067004
H	-0.213831	4.652543	-0.505865
H	0.811467	4.494601	0.947905
H	1.524370	4.365481	-0.665848
N	1.045154	1.949460	0.908427
N	0.675397	0.572531	0.745299
H	0.215672	0.261744	1.607494
C	1.739368	-0.351425	0.437821
C	2.865667	0.070928	-0.270477
C	1.591580	-1.692952	0.804241
C	3.845181	-0.860649	-0.611436
H	2.969020	1.121474	-0.514008
C	2.580236	-2.615206	0.461266
H	0.710437	-2.012927	1.355832
C	3.709227	-2.203211	-0.248922
H	4.725753	-0.531445	-1.156278
H	2.467076	-3.655368	0.754158
H	4.480961	-2.921212	-0.511318

TS-*cis*			
H	-2.803202	-3.747983	1.087926
C	-2.018888	-3.138058	0.647191
C	-0.890524	-2.798033	1.397674
C	-2.138611	-2.689966	-0.670824
C	0.115230	-2.014820	0.834324
H	-0.796980	-3.142511	2.424362
C	-1.132561	-1.906063	-1.231676
H	-3.013121	-2.954588	-1.259467
C	0.011646	-1.565752	-0.492023
H	0.997603	-1.745197	1.407221
H	-1.223602	-1.561839	-2.260046
C	1.079102	-0.718941	-1.094236
H	0.892239	-0.589867	-2.165925
C	2.941983	0.274916	0.005878
C	2.466728	-0.858068	-0.624662
H	2.890106	-1.837194	-0.431214
C	4.279584	0.368006	0.686676
H	4.978294	0.966100	0.089083
H	4.177811	0.863513	1.658243
H	4.719741	-0.622664	0.833158
N	2.137254	1.356518	0.111739
N	1.019152	1.061400	-0.717562
C	-0.243326	1.604957	-0.259650
C	-0.481492	1.737708	1.106735
C	-1.219242	1.944534	-1.197158
C	-1.716256	2.224601	1.533530
H	0.313267	1.484703	1.798156
C	-2.453161	2.425788	-0.759810
H	-1.016529	1.841830	-2.261384
C	-2.703952	2.565815	0.606381
H	-1.906606	2.339780	2.596977
H	-3.213659	2.695693	-1.487093
H	-3.663965	2.943778	0.946663
H	1.196196	1.401279	-1.665994

2-*trans*			
H	4.771945	-2.206447	-0.405687
C	3.903733	-1.592385	-0.181229
C	3.741054	-0.352337	-0.804531
C	2.953038	-2.034017	0.740794
C	2.633084	0.440770	-0.507869
H	4.485426	0.002527	-1.512666
C	1.840301	-1.242589	1.030111
H	3.078120	-2.993192	1.236434
C	1.665136	0.000252	0.406664
H	2.512910	1.422637	-0.958718
H	1.100875	-1.587648	1.749304
C	0.443627	0.846888	0.700446
H	-0.059986	0.438730	1.593449
C	-0.508338	2.850819	0.003971
C	0.563189	2.339444	0.689321
H	1.219875	2.880867	1.356095
C	-0.867518	4.307275	-0.095416
H	-0.160370	4.927137	0.462305
H	-0.877095	4.634703	-1.141364
H	-1.874120	4.479069	0.303673
N	-1.325452	1.982510	-0.647068
N	-0.617994	0.691563	-0.459265
H	-0.059558	0.534566	-1.308742
C	-1.528431	-0.448120	-0.309218
C	-2.726670	-0.275063	0.379170
C	-1.166525	-1.686066	-0.837406
C	-3.569625	-1.372375	0.551305
H	-2.984995	0.716498	0.731022
C	-2.019917	-2.777001	-0.661167
H	-0.231362	-1.801922	-1.378183
C	-3.219228	-2.622827	0.035371
H	-4.509588	-1.246074	1.081116
H	-1.745638	-3.743907	-1.073157
H	-3.883781	-3.472076	0.167543

2-*cis*			
H	1.120623	4.466673	1.023763
C	0.675660	3.579595	0.580282
C	-0.376206	2.925016	1.226148
C	1.147730	3.095655	-0.640812
C	-0.956522	1.793895	0.653160
H	-0.749649	3.301679	2.175004
C	0.572077	1.957092	-1.205678
H	1.958820	3.605499	-1.154203
C	-0.483927	1.294315	-0.567570
H	-1.791021	1.294047	1.134320
H	0.941769	1.581863	-2.157950
C	-1.110691	0.069122	-1.205558
H	-0.779716	0.019430	-2.250224
C	-2.683075	-1.113433	0.042505
C	-2.570130	-0.169829	-0.948704
H	-3.337015	0.532645	-1.245696
C	-3.953233	-1.494695	0.750249
H	-4.226594	-2.532978	0.528521
H	-3.818823	-1.424805	1.835935
H	-4.781454	-0.844098	0.456081
N	-1.551029	-1.761035	0.430185
N	-0.593951	-1.309698	-0.589179
C	0.803821	-1.371917	-0.158964
C	1.119668	-1.224401	1.187693
C	1.793075	-1.570610	-1.120355
C	2.460402	-1.264461	1.571187
H	0.311663	-1.108373	1.899022
C	3.130781	-1.609151	-0.726234
H	1.525858	-1.698421	-2.167367
C	3.465449	-1.452836	0.620119
H	2.718794	-1.154380	2.620556
H	3.906724	-1.766198	-1.469952
H	4.506880	-1.486336	0.927746
H	-0.701298	-1.951251	-1.387412

4.3 Pentadienyl anion C

1			
C	0.001800	2.177299	0.013931
C	1.269112	1.547564	0.037887
H	2.099003	2.251260	0.147773
C	1.639910	0.219745	-0.102479
H	0.874978	-0.517519	-0.325074
C	-0.005654	3.699221	0.056502
H	0.915632	4.126567	-0.361290
H	-0.106603	4.110855	1.076944
H	-0.843068	4.114839	-0.522555
C	-2.986735	-0.284920	0.084628
C	-4.100367	0.444747	-0.420487
H	-3.947212	1.452926	-0.796305
C	-5.376834	-0.103018	-0.466395
H	-6.196139	0.497510	-0.861411
C	-5.623551	-1.410833	-0.029502
H	-6.623455	-1.836291	-0.074671
C	-4.542856	-2.158776	0.455178
H	-4.700729	-3.181401	0.796937
C	-3.266008	-1.614081	0.509698
H	-2.443454	-2.213723	0.896412
C	2.987323	-0.289707	-0.069111
C	3.235186	-1.652594	-0.397228
H	2.386612	-2.277472	-0.671425
C	4.511859	-2.200101	-0.386046
H	4.643467	-3.249378	-0.649203
C	5.625232	-1.421989	-0.044087
H	6.625419	-1.849017	-0.033572
C	5.411380	-0.079229	0.293331
H	6.257532	0.547876	0.574067
C	4.136006	0.472610	0.288603
H	4.013877	1.512830	0.578831
C	-1.643526	0.229715	0.173966
H	-0.893263	-0.490475	0.486714
C	-1.267222	1.549473	-0.013154
H	-2.092936	2.249848	-0.173585

TS-*cis*			
C	3.050350	-0.001963	-0.023423
C	2.360614	-1.185607	-0.301696
H	2.605663	-2.111596	0.220347
C	1.053534	-0.986032	-0.939859
H	1.022540	-1.028924	-2.035247
C	4.407436	-0.002773	0.641644
H	4.541980	-0.891922	1.274008
H	4.543062	0.886207	1.274018
H	5.230492	-0.003270	-0.089311
C	1.054769	0.984607	-0.939942
C	2.362125	1.182506	-0.301806
H	2.608609	2.108380	0.219757
H	1.023796	1.027462	-2.035334
C	-0.115753	-1.725187	-0.398925
C	-1.209316	-2.076572	-1.217427
C	-0.209604	-2.057457	0.968666
C	-2.324931	-2.737654	-0.708663
H	-1.166044	-1.827602	-2.277173
C	-1.319012	-2.727931	1.479759
H	0.617851	-1.776641	1.614979
C	-2.388848	-3.073521	0.647870
H	-3.148518	-2.998556	-1.372591
H	-1.356418	-2.976569	2.540016
H	-3.260789	-3.585911	1.050358
C	-0.113532	1.725321	-0.399025
C	-1.206780	2.077841	-1.217469
C	-0.206817	2.058010	0.968506
C	-2.321540	2.740361	-0.708707
H	-1.163941	1.828580	-2.277164
C	-1.315354	2.729932	1.479588
H	0.620382	1.776344	1.614777
C	-2.384886	3.076609	0.647759
H	-3.144902	3.002095	-1.372588
H	-1.352323	2.978858	2.539793
H	-3.256167	3.590124	1.050245

2-*cis*			
C	0.269233	-1.480762	-0.563482
C	3.791388	-2.122453	0.652980
H	4.053015	-3.105709	0.232166
H	3.697612	-2.255767	1.739419
H	4.643123	-1.454500	0.465517
C	2.511558	-1.580559	0.060377
C	2.486411	-0.670585	-0.993421
H	3.310274	0.006412	-1.223278
C	1.040046	-0.237320	-1.197446
C	-1.173197	-1.221821	-0.168869
C	-1.537488	-0.983749	1.164161
H	-0.740470	-0.998949	1.903635
C	-2.865771	-0.743822	1.519931
H	-3.121133	-0.563337	2.563369
C	-3.868962	-0.737109	0.547722
H	-4.905643	-0.551655	0.824218
C	-3.525646	-0.980202	-0.784831
H	-4.296609	-0.983904	-1.554388
C	-2.195716	-1.223493	-1.131289
H	-1.936737	-1.426694	-2.169973
C	1.230670	-1.962042	0.504141
H	1.049156	-2.923147	0.992908
H	0.225227	-2.200540	-1.415425
C	0.740291	1.113122	-0.548588
C	1.194451	1.417651	0.748200
C	0.054657	2.113493	-1.249119
C	0.949070	2.665476	1.319830
H	1.719943	0.642333	1.295428
C	-0.172960	3.378116	-0.690082
H	-0.303505	1.898645	-2.255248
C	0.269030	3.658150	0.600403
H	1.293871	2.871834	2.332278
H	-0.694028	4.140806	-1.267858
H	0.091472	4.636598	1.044335
H	0.732053	-0.144978	-2.250792