Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2014

Electronic Supplementary Information (ESI) for: Solvent Effects on the Photochemistry of 4-aminoimidazole-5-carbonitrile, a Prebiotically Plausible Precursor of Purines

Rafał Szabla,[*a] **Robert W. Góra,**[*b] **Judit E. Šponer,**[a] **Andrzej L. Sobolewski,**[c] **and Jiří Šponer**[a]

June 17, 2014

Electric dipole moment vectors of the selected electronic states of 1H-AICN and 3H-AICN.

Fig. 1 Electric dipole moment vectors of the selected electronic states of 1H-AICN computed at the CASPT2//SA-CASSCF/aug-cc-pVDZ level (as described in the article). The green vector corresponds to the ground state, the black one to the $^1\pi\sigma^*$ state, and the red vector corresponds to the $^1\pi\pi^*$ state.

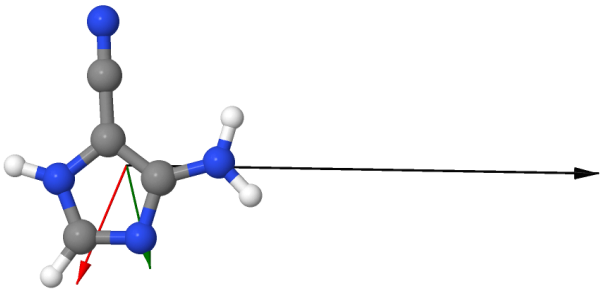


Fig. 2 Electric dipole moment vectors of the selected electronic states of 3H-AICN computed at the CASPT2//SA-CASSCF/aug-cc-pVDZ level (as described in the article). The green vector corresponds to the ground state, the black one to the $^1\pi\sigma^*$ state, and the red vector corresponds to the $^1\pi\pi^*$ state.

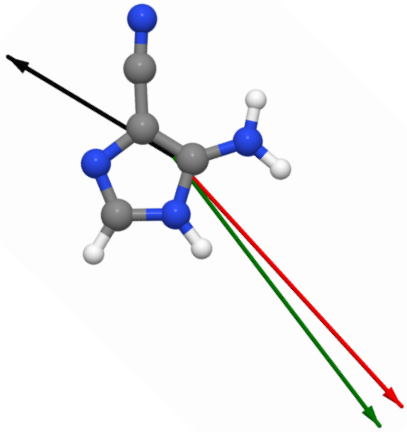
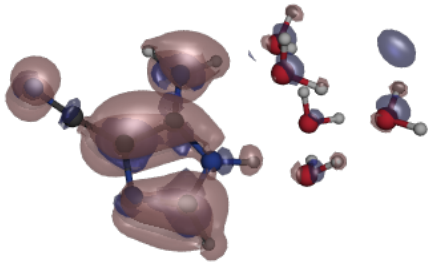
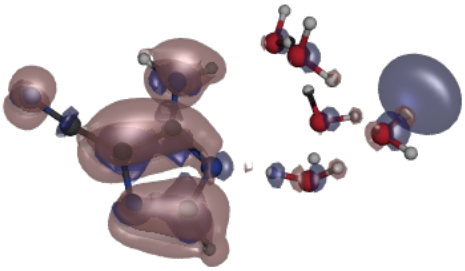


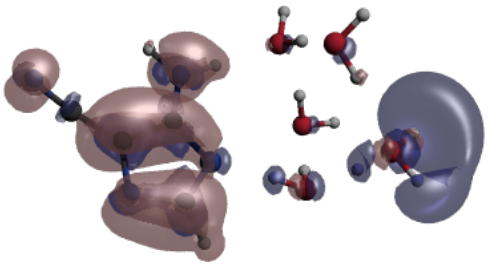
Fig. 3 Plots of differences in the electronic density distributions of 3H-AICN cluster with five water molecules in the excited $^1\pi\sigma^*$ and the ground state ($\rho_{S_1} - \rho_{S_0}$), calculated at the CASPT2//SA2-CASSCF(2,2)/aug-cc-pVDZ level for selected stationary points: equilibrium geometry in the S_1 state before (a) and after (b) the first proton transfer and at the S_1/S_0 conical intersection (c). The isodensity surfaces were plotted for ± 0.002 e/bohr^3. Blue surfaces indicate regions of increased electronic density and red the opposite. According to Mulliken population analysis, the charge transferred in the S_1 state from the AICN chromophore towards the water molecules amounts to 1.09e, 1.04e and 1.00e for a, b and c structres respectively.



a)



b)



c)

Cartesian coordinates of the stationary points considered in the article

Ground-state geometries of the considered AICN tautomers optimized at the MP2/aug-cc-pVDZ level

1H-AICN, C_1 symmetry

C	0.163217	0.047436	1.269394
C	2.116500	0.061844	0.410998
C	1.226539	-0.012411	-0.645189
C	1.453745	-0.063504	-2.023879
N	-0.018310	-0.020603	-0.064243
N	3.489184	0.028828	0.369927
N	1.443204	0.098760	1.586720
N	1.674858	-0.099092	-3.172177
H	-0.654942	0.059221	1.963560
H	3.901560	0.375810	-0.479842
H	3.912984	0.413516	1.197865
H	-0.893969	-0.066777	-0.554475

1H-AICN, C_s symmetry

N	-0.051871	-1.600008	0.000000
C	-1.332430	-1.279746	0.000000
N	-1.515862	0.054197	0.000000
C	-0.269802	0.636766	0.000000
C	0.621608	-0.422412	0.000000
N	1.977074	-0.380790	0.000000
C	-0.038434	2.014481	0.000000
N	0.194144	3.161312	0.000000
H	-2.150048	-1.974662	0.000000
H	2.472018	0.487487	0.000000
H	2.485969	-1.241225	0.000000
H	-2.392365	0.544598	0.000000

3H-AICN, C_1 symmetry

C	0.075543	-0.010271	1.257018
C	2.127551	0.048955	0.463273
C	1.194681	0.016502	-0.550172
C	1.504633	0.022870	-1.924091
N	-0.079556	-0.027408	-0.045265
N	1.392641	0.026832	1.607285
N	3.514087	0.023397	0.472214
N	1.839014	0.033121	-3.044099
H	1.772620	-0.013406	2.536812
H	-0.714496	-0.016655	1.983056
H	3.876794	-0.158806	-0.452905
H	3.924043	0.877898	0.822150

3H-AICN, C_s symmetry

N	-0.331605	-1.314784	0.000000
C	-1.655194	-0.951738	0.000000
N	-1.798483	0.346966	0.000000
C	-0.517901	0.847069	0.000000
C	0.407652	-0.175108	0.000000
N	1.765450	-0.139483	0.000000
C	-0.185186	2.212447	0.000000
N	0.185971	3.321445	0.000000
H	0.024452	-2.253717	0.000000
H	-2.445639	-1.677007	0.000000
H	2.224948	0.749967	0.000000
H	2.325534	-0.966057	0.000000

Conical intersections for the N–H bond stretching mechanisms of the considered AICN tautomers optimized at the MR-CISD/SA-2-CASSCF(2,2)/cc-pVDZ level (See Fig. 2 of the article for reference)

1H-AICN, Fig. 2 a)

N	-1.620007	0.072792	-0.001300
N	-0.044289	-1.596569	0.013906
N	0.500734	3.046965	-0.044848
N	1.978144	-0.342690	-0.017026
C	-0.340096	0.626840	-0.001575
C	0.613728	-0.420715	0.013362
C	-1.332040	-1.273091	-0.000408
C	0.037527	1.989329	-0.023501
H	-2.060125	-2.071686	-0.013898
H	2.438276	0.524305	0.201698
H	2.510927	-1.169448	0.203034
H	-3.130344	0.957495	0.000000

1H-AICN, Fig. 2 b)

N	-0.065837	-1.613121	-0.000000
N	-1.492438	0.079349	0.000000
N	1.997411	-0.484389	0.000000
N	-0.103355	3.221232	-0.000000
C	-1.311812	-1.265006	-0.000000
C	-0.243051	0.650090	0.000000
C	0.671133	-0.438731	0.000000
C	-0.114462	2.066333	-0.000000
H	-2.151504	-1.946767	-0.000000
H	2.412331	0.444341	0.000000
H	2.944302	-2.016171	0.000000
H	-2.367446	0.572650	0.000000

1H-AICN, Fig. 2 c)

N	-0.079060	-1.630085	-0.000000
N	-1.546194	0.041316	0.000000
N	1.964425	-0.249159	0.000000
N	0.474109	3.055938	0.000000
C	-1.343465	-1.297732	0.000000
C	-0.296225	0.617501	-0.000000
C	0.625911	-0.424576	-0.000000
C	0.047117	1.983968	0.000000
H	-2.190645	-1.980072	0.000000
H	2.917997	1.269865	0.000000
H	2.444140	-1.147796	0.000000
H	-2.429947	0.517453	0.000000

3H-AICN, Fig. 2 d)

C	-1.650923	-0.951417	-0.000000
C	-0.493651	0.832691	0.000000
C	0.403927	-0.247106	-0.000000
C	-0.130983	2.228859	-0.000000
N	-0.311742	-1.435735	-0.000000
N	-1.765684	0.349697	0.000000
N	1.739767	-0.089999	0.000000
N	0.232969	3.327579	-0.000000
H	0.324360	-3.044584	0.000000
H	-2.548326	-1.549466	0.000000
H	2.095753	0.849551	0.000000
H	2.364099	-0.862802	0.000000

3H-AICN, Fig. 2 e)

N	-0.331521	-1.322573	0.000000
N	-1.784791	0.363609	0.000000
N	1.747172	-0.204472	-0.000000
N	0.093346	3.365364	0.000001
C	-1.628800	-0.939654	-0.000000
C	-0.527297	0.862654	-0.000000
C	0.455819	-0.181675	0.000000
C	-0.217801	2.254601	0.000001
H	0.024684	-2.260925	-0.000001
H	-2.443578	-1.650855	0.000000
H	2.149536	0.725504	-0.000000
H	2.747111	-1.588221	0.000000

3H-AICN, Fig. 2 f)

N	-0.340754	-1.345382	0.000000
N	-1.786450	0.349737	-0.000000
N	1.754862	-0.070082	0.000000
N	0.152810	3.323319	0.000000
C	-1.646457	-0.945187	-0.000000
C	-0.514091	0.837114	0.000000
C	0.455409	-0.202426	0.000000
C	-0.179763	2.218939	-0.000000
H	-0.030088	-2.299689	0.000000
H	-2.468121	-1.651175	-0.000000
H	2.591613	1.459721	0.000000
H	2.265547	-0.946332	0.000000

Conical intersections for the ring-puckering mechanisms of the considered AICN tautomers optimized at the MR-CISD/SA-2-CASSCF(2,2)/cc-pVDZ level

1H-AICN

C	-0.237402	0.590857	0.401350
C	-0.320579	1.721221	-0.454290
C	0.670601	-0.568178	0.064157
C	-1.334558	-1.075312	-0.110653
N	2.002178	-0.469158	0.095392
N	-0.031318	-1.604971	-0.226253
N	-1.413081	-0.097763	0.914681
N	-0.339385	2.700152	-1.073760
H	2.555598	-1.237119	-0.237664
H	-2.057404	-1.165218	-0.918628
H	-2.245107	0.473616	0.847575
H	2.436532	0.423715	0.223951

3H-AICN

N	1.733248	-0.227680	0.059949
N	-1.689058	0.428881	0.235932
N	-0.337170	-1.067144	-0.987593
N	0.034878	3.490514	-0.258143
C	0.388646	-0.197803	-0.151831
C	-0.539393	0.991785	-0.000582
C	-1.351685	-0.899644	0.085620
C	-0.262937	2.379701	-0.156508
H	2.173320	-1.130245	-0.014581
H	2.044098	0.288128	0.869243
H	-1.971482	-1.726277	0.401886
H	0.051614	-2.004245	-0.938025

3H-AICN water clusters optimized at the ADC(2)/aug-cc-pVDZ level

3H-AICN-W1 protonated

C	-1.83271	-0.25773	0.09913
C	0.23775	0.02230	-0.55203
C	-0.66305	-0.12826	-1.68350
C	-0.25286	-0.09797	-3.05019
N	-1.93260	-0.29942	-1.25757
N	-0.57011	-0.06969	0.55180
N	1.54915	0.20821	-0.54030
N	0.17665	-0.05968	-4.15601
H	-0.23313	-0.00118	1.57277
H	-2.68102	-0.36422	0.77304
H	2.06760	0.26368	-1.42023
H	2.06908	0.29976	0.35648
O	0.28386	0.10126	3.03680
H	0.78112	0.94218	3.12186
H	1.00026	-0.55923	3.14797

3H-AICN-W1 deprotonated

N	-0.59046	-0.08680	0.59379
C	-1.83706	-0.23082	0.10453
N	-1.95035	-0.25327	-1.27388
C	-0.67982	-0.11332	-1.67985
C	0.19704	-0.00667	-0.52238
N	1.52440	0.13873	-0.51508
C	-0.23318	-0.07458	-3.03720
N	0.25342	-0.02916	-4.11878
O	0.35976	0.00961	3.02242
H	-0.05138	-0.01327	2.04184
H	-2.70895	-0.32463	0.75139
H	2.03938	0.18758	-1.39105
H	2.03828	0.18962	0.37251
H	0.49019	0.97001	3.26917
H	1.32783	-0.32661	2.92528

3H-AICN-W2 protonated

N	-0.46851	0.04209	1.24851
C	-1.66871	-0.46026	0.87263
N	-1.79237	-0.65329	-0.46787
C	-0.60344	-0.24866	-0.96459
C	0.27098	0.20310	0.10084
N	1.51082	0.65932	0.02827
C	-0.24039	-0.26399	-2.34542
N	0.15503	-0.24210	-3.46377
O	0.37072	0.54897	3.69929
O	2.69004	1.33387	2.38002
H	-0.16048	0.28357	2.24780
H	-2.45519	-0.68397	1.59141
H	1.94970	0.75281	-0.88976
H	2.04973	0.95627	0.88626
H	0.02126	1.30353	4.20153
H	1.30795	0.80162	3.52966
H	2.77162	2.31407	2.49132
H	3.59990	1.00798	2.56837

3H-AICN-W2 deprotonated

C	0.22568	0.17983	0.10196
N	-0.46578	0.02347	1.27566
C	-1.66007	-0.47077	0.89211
N	-1.82721	-0.66394	-0.46407
C	-0.65198	-0.25984	-0.97043
C	-0.29167	-0.25766	-2.35389
N	0.12298	-0.21201	-3.46464
N	1.47478	0.63581	-0.01069
O	0.47756	0.56603	3.59247
O	2.72324	1.33175	2.52472
H	0.01725	0.35874	2.63461
H	-2.44925	-0.70405	1.60639
H	1.88679	0.73313	-0.93641
H	2.02124	0.93022	0.81273
H	0.12886	1.42366	3.94492
H	1.44602	0.79229	3.35608
H	2.68020	2.30249	2.72984
H	3.58976	1.05532	2.89642

3H-AICN-W3 protonated

C	-2.26812	-1.20703	-0.36974
C	-0.46672	-0.04708	-0.79663
C	-0.93527	-0.75572	-1.97190
C	-0.29025	-0.68671	-3.24422
N	-2.04635	-1.46604	-1.68915
N	-1.36634	-0.36428	0.18521
N	0.58114	0.75687	-0.68220
N	0.31890	-0.53902	-4.25174
H	-1.34849	-0.04129	1.21080
H	-3.08998	-1.63300	0.20271
H	1.18559	0.87362	-1.49509
H	0.90431	1.10901	0.24836
O	1.14653	-1.39760	1.57413
H	0.66032	-1.80605	2.32786
H	1.96633	-1.92761	1.54186
O	1.26202	1.25457	1.90754
H	1.45330	0.28603	2.02533
H	1.96577	1.72229	2.38394
O	-1.38071	0.55257	2.65914
H	-1.36346	-0.14009	3.34835
H	-0.51265	0.99633	2.76319

3H-AICN-W3 deprotonated

N	-1.62196	-0.31203	-0.04910
C	-2.68854	-0.80931	-0.70338
N	-2.55803	-0.93798	-2.07558
C	-1.31225	-0.49344	-2.29567
C	-0.70004	-0.09670	-1.03797
N	0.52669	0.40368	-0.85939
C	-0.66124	-0.40482	-3.56568
N	-0.01566	-0.27643	-4.55296
O	-1.20149	0.16055	2.49699
O	1.24579	0.97971	1.86572
O	2.24151	-1.27879	2.79735
H	-1.42550	-0.09647	1.50550
H	-3.60353	-1.09865	-0.18726
H	1.14546	0.49190	-1.66169
H	0.87854	0.64848	0.07773
H	1.39678	-1.74456	3.00102
H	2.69313	-1.27998	3.65911
H	1.73754	0.19779	2.26584
H	1.63379	1.76858	2.27561
H	-1.04056	-0.69634	3.02231
H	-0.28518	0.58418	2.43769

3H-AICN-W4 protonated

C	-2.31063	-1.11807	-0.35302
C	-0.45595	-0.05079	-0.77800
C	-0.93599	-0.76706	-1.94341
C	-0.26676	-0.75885	-3.20542
N	-2.08008	-1.42249	-1.66248
N	-1.38204	-0.30419	0.19858
N	0.62273	0.71203	-0.66757
N	0.36967	-0.66724	-4.20235
H	-1.37795	0.03683	1.23512
H	-3.16391	-1.48869	0.21263
H	1.23607	0.79485	-1.47773
H	0.94121	1.07924	0.26109
O	1.03776	-1.45782	1.56649
H	0.55787	-1.75842	2.37334
H	1.86805	-1.96174	1.61324
O	1.22064	1.23502	1.91100
H	1.37457	0.26703	2.05604
H	1.89457	1.68101	2.44904
O	-1.48474	0.52690	2.65685
H	-1.28952	-0.21419	3.27657
H	-0.71692	1.11669	2.78440
O	-0.40989	-1.66936	3.95557
H	-0.79612	-2.46840	4.36339
H	0.28966	-1.39766	4.59256

3H-AICN-W4 deprotonated

N	-1.47362	-0.32293	0.15100
C	-2.40349	-1.09411	-0.44619
N	-2.20025	-1.36790	-1.78664
C	-1.05476	-0.72192	-2.04864
C	-0.57321	-0.06212	-0.84745
N	0.53001	0.68283	-0.72758
C	-0.38290	-0.67360	-3.31009
N	0.26609	-0.55039	-4.29541
O	-1.28763	0.48678	2.62096
O	1.19596	1.15499	2.02985
O	1.42499	-1.48831	1.82134
O	-0.47609	-1.56102	3.95788
H	-1.42436	0.12725	1.64640
H	-3.26889	-1.48222	0.09045
H	1.14168	0.79005	-1.53343
H	0.84223	1.03694	0.18561
H	0.85154	-1.81104	2.55018
H	2.25973	-1.96089	1.96960
H	1.49240	0.20410	2.09922
H	1.74703	1.64346	2.66317
H	-1.12133	-0.31871	3.23177
H	-0.38310	0.92601	2.57381
H	-1.04343	-2.27103	4.33044
H	0.08538	-1.27817	4.72544

3H-AICN-W5 protonated

C	-2.35970	-0.79175	-0.68604
C	-0.34272	-0.04235	-1.02949
C	-0.90016	-0.64054	-2.22862
C	-0.20008	-0.71432	-3.47198
N	-2.14488	-1.10128	-1.99825
N	-1.32436	-0.16556	-0.08288
N	0.84648	0.52727	-0.88857
N	0.47494	-0.71025	-4.44737
H	-1.35055	0.13968	0.97890
H	-3.28127	-1.02086	-0.15310
H	1.46698	0.53500	-1.69799
H	1.21740	0.86800	0.03103
O	0.84240	-1.44804	1.61169
H	0.47261	-1.56120	2.51685
H	1.62241	-2.02774	1.62360
O	1.66959	1.18319	1.61665
H	1.51485	0.24956	1.90805
H	2.53238	1.40389	2.01315
O	-1.71131	0.53165	2.33878
H	-1.33279	-0.01874	3.05824
H	-1.37564	1.44263	2.53317
O	-0.24430	-1.02841	4.13557
H	-0.48943	-1.64038	4.85230
H	0.51050	-0.52044	4.51035
O	-0.40348	2.88492	2.56754
H	0.44269	2.42170	2.39820
H	-0.27764	3.29941	3.43356

3H-AICN-W5 deprotonated

N	-1.36606	-0.15425	-0.13429
C	-2.39081	-0.80265	-0.72247
N	-2.22195	-1.14168	-2.05355
C	-0.99713	-0.66621	-2.32094
C	-0.43575	-0.04469	-1.13344
N	0.76105	0.53984	-1.03457
C	-0.31624	-0.74790	-3.57608
N	0.35255	-0.74633	-4.55583
O	-1.75676	0.63017	2.34671
O	-0.25823	2.62964	2.79619
O	1.81487	1.26356	1.50080
O	1.35675	-1.33587	1.95355
O	-0.52420	-0.96482	4.00386
H	-1.52746	0.32189	1.38948
H	-3.30698	-1.04761	-0.18489
H	1.36505	0.54651	-1.85360
H	1.13757	0.89493	-0.14165
H	0.76431	-1.40312	2.73454
H	2.08863	-1.93258	2.17181
H	1.77870	0.32139	1.82016
H	2.68458	1.58840	1.77882
H	-1.39536	-0.04572	3.01049
H	-1.21695	1.49392	2.54737
H	-0.96909	-1.61643	4.58570
H	-0.03038	-0.38431	4.64371
H	0.58645	2.25443	2.45535
H	-0.11064	2.70255	3.75709

3H-AICN-W6 protonated

N	-1.25177	-0.18307	-0.25064
C	-2.35548	-0.79003	-0.74143
N	-2.25292	-1.18150	-2.04621
C	-1.01082	-0.79257	-2.39187
C	-0.34070	-0.15679	-1.27183
N	0.88500	0.35026	-1.24469
C	-0.40549	-0.97150	-3.67379
N	0.20013	-1.05811	-4.69005
O	-1.58735	0.67131	2.09898
O	-1.73366	3.33929	1.94932
O	1.93370	1.03452	1.14534
O	0.86118	-1.40436	1.69441
O	0.07729	-0.30923	4.09571
H	-1.21618	0.20300	0.79085
H	-3.24363	-0.94319	-0.13027
H	1.44029	0.28939	-2.09792
H	1.34244	0.70679	-0.36800
H	0.58467	-1.27213	2.63116
H	1.53816	-2.09716	1.75971
H	1.67806	0.16244	1.54493
H	2.85663	1.15769	1.43282
H	-1.06144	0.41285	2.88662
H	-1.71233	1.65417	2.14998
H	-0.18523	-0.70088	4.94882
H	0.88324	0.21154	4.32063
H	-0.79039	3.52706	2.17809
H	-2.25609	3.90526	2.53174
O	0.93584	3.43652	2.41447
H	1.25200	2.58529	2.05067
H	1.25215	3.40841	3.33142

3H-AICN-W6 deprotonated

C	-0.50401	-0.17666	-1.39793
N	-1.39561	-0.17800	-0.35833
C	-2.51232	-0.70632	-0.89797
N	-2.44162	-1.06561	-2.23267
C	-1.18321	-0.73344	-2.55580
C	-0.57051	-0.89773	-3.83770
N	0.05212	-0.97784	-4.84417
N	0.75794	0.25654	-1.34967
O	-1.84088	0.71646	2.07759
O	-1.54078	3.21545	2.05186
O	2.13450	1.01088	0.98777
O	1.07265	3.19828	2.52676
O	1.76750	-1.28532	2.30513
O	-0.29318	-0.26273	3.92771
H	-1.53597	0.37221	1.16177
H	-3.42585	-0.84406	-0.31927
H	1.32090	0.19095	-2.19511
H	1.21384	0.58098	-0.47820
H	1.08186	-1.06707	2.97401
H	2.47532	-1.68757	2.83016
H	2.11453	0.18073	1.53907
H	3.06796	1.26710	0.95766
H	-1.26707	0.32638	2.81997
H	-1.75324	1.75483	2.10589
H	-0.71870	-0.76972	4.65330
H	0.17116	0.47083	4.41879
H	-0.56844	3.32090	2.26091
H	-2.00667	3.71314	2.73929
H	1.43908	2.42441	2.05073
H	1.21747	2.97190	3.46360

Two-body-dissociation conical intersection of the 3H-AICN cluster with one water molecule, optimized at the MR-CISD/SA-2-CASSCF(2,2)/cc-pVDZ level

```
3H-AICN-W1 conical intersection

 N    -0.572499    -0.081097     0.587229
 N    -1.930338    -0.255495    -1.259598
 N     1.514483     0.136191    -0.511667
 N     0.187548    -0.034939    -4.101459
 C    -1.808733    -0.230198     0.084001
 C    -0.673755    -0.111740    -1.670138
 C     0.182265    -0.005915    -0.516261
 C    -0.240479    -0.075237    -3.031325
 O     0.836752     0.087687     4.320989
 H     0.455819     0.071588     3.414906
 H    -2.679700    -0.325485     0.718926
 H     2.027982     0.188879    -1.369944
 H     2.002471     0.174283     0.361521
 H     0.943137     1.031538     4.562327
 H     1.876349    -0.321796     4.230648
```