

## Supporting Information

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### Augmentation of inductive effects through short range intramolecular hydrogen bonds for the improvement of cooperativity of trimeric rosettes

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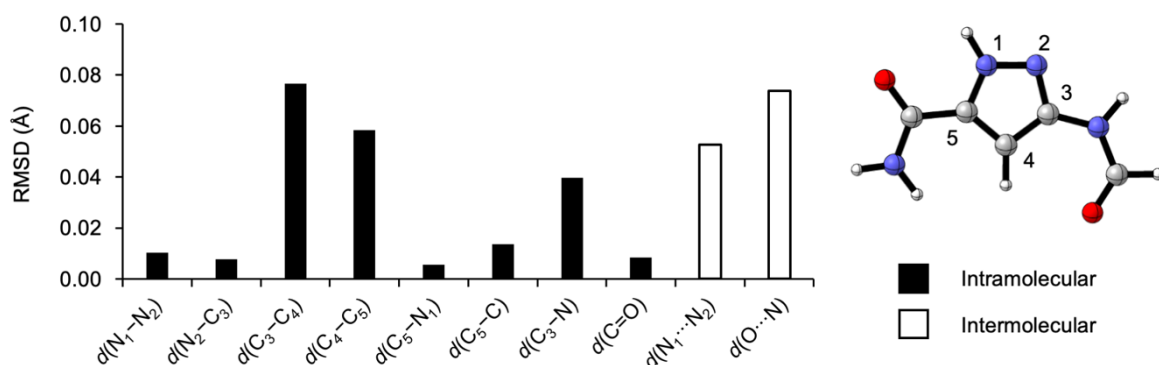
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**Figure S1.** Average RMSDs (in Å) for relevant interatomic distances of (b-P35)<sub>3</sub> trimer relative to the experimental X-ray structure.

**Table S1.** Bonding analysis of trimers (in kcal mol<sup>-1</sup>) computed at BLYP-D3(BJ)/6-311++G(d,p)

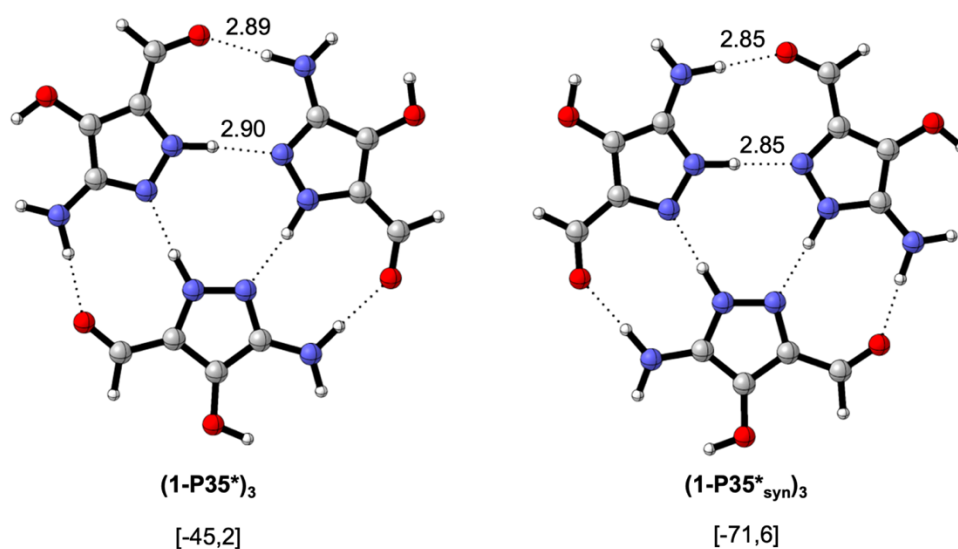
Trimer	$\Delta E_{\text{bond}}$	$\Delta E_{\text{strain}}$	$\Delta E_{\text{int}}$	$\Delta E_{\text{coop}}$
(a-P35) <sub>3</sub>	-39.9	2.8	-42.8	0.4
(b-P35) <sub>3</sub>	-43.9	3.5	-47.4	0.3
(c-P35) <sub>3</sub>	-51.2	4.2	-55.5	0.2
(a-P35 <sub>syn</sub> ) <sub>3</sub>	-63.1	2.1	-65.3	-12.6
(b-P35 <sub>syn</sub> ) <sub>3</sub>	-76.0	2.9	-78.9	-13.7
(c-P35 <sub>syn</sub> ) <sub>3</sub>	-86.5	5.2	-91.7	-17.4

**Table S2.** Local molecular orbital energy decomposition analysis (LMOEDA) of trimers (in kcal mol<sup>-1</sup>) computed at BLYP-D3(BJ)/6-311++G(d,p).

Trimer	$\Delta E_{\text{int}}$	$\Delta E_{\text{ele}}$	$\Delta E_{\text{ex}}$	$\Delta E_{\text{rep}}$	$\Delta E_{\text{ex+rep}}$	$\Delta E_{\text{pol}}$	$\Delta E_{\text{disp}}$
(a-P35) <sub>3</sub>	-47.1	-54.1	-17.7	112.7	95.0	-67.7	-20.2
(b-P35) <sub>3</sub>	-52.4	-48.0	-18.6	119.2	100.6	-83.7	-21.4
(c-P35) <sub>3</sub>	-60.7	-53.6	-21.2	133.1	111.9	-96.3	-22.7
(a-P35 <sub>syn</sub> ) <sub>3</sub>	-69.8	-67.4	-19.4	121.7	102.3	-83.2	-21.5
(b-P35 <sub>syn</sub> ) <sub>3</sub>	-84.1	-69.1	-22.1	137.0	114.9	-106.5	-23.4
(c-P35 <sub>syn</sub> ) <sub>3</sub>	-97.3	-79.1	-26.7	160.5	133.8	-126.6	-25.5

**Table S3.** Average distances (in Å) between heavy atoms of N-H...N and N-H...O hydrogen bonds within the trimers. Computed at BLYP-D3(BJ)/6-311++G(d,p).

Trimer	$d(N...N)$	$d(N...O)$
(a-P35) <sub>3</sub>	2.905	2.908
(b-P35) <sub>3</sub>	2.965	2.797
(c-P35) <sub>3</sub>	2.900	2.697
(a-P35 <sub>syn</sub> ) <sub>3</sub>	2.885	2.874
(b-P35 <sub>syn</sub> ) <sub>3</sub>	2.918	2.755
(c-P35 <sub>syn</sub> ) <sub>3</sub>	2.899	2.697



**Figure S2.** Molecular structures of  $(1\text{-P35}^*)_3$  and  $(1\text{-P35}^*_{\text{syn}})_3$  trimers with  $R_3 = \text{OH}$  optimized at BLYP-D3(BJ)/6-311++G(d,p). Interaction energies (between brackets) are in kcal mol<sup>-1</sup> and hydrogen bond distances (N/O...N) are in Å.

**Table S4.** Cartesian coordinates (in Å) and total electronic energy (in Hartrees) of all monomers and trimers optimized at BLYP-D3(BJ)/6-311++G(d,p).

a-P35 monomer

HF = -394.9069024

H	-2.063517	0.215040	0.000000
C	0.000000	0.755697	0.000000
C	1.129355	-0.079521	0.000000
C	0.601739	-1.400404	0.000000
N	-0.756477	-1.393825	0.000000
N	-1.089640	-0.073717	0.000000
H	2.168592	0.231521	0.000000
H	0.835036	2.767424	0.000000
H	2.298294	-2.617173	0.000000
O	-1.213462	2.800534	0.000000
C	-0.132024	2.210686	0.000000
N	1.288894	-2.596858	0.000000
H	0.775433	-3.469024	0.000000

a-P35<sub>syn</sub> monomer

HF = -394.8947621

H	-1.678330	-1.851681	0.000000
C	0.438947	-1.451829	0.000000
C	1.069529	-0.209199	0.000000
C	0.000000	0.743495	0.000000
N	-1.213285	0.153452	0.000000
N	-0.913872	-1.182246	0.000000
N	0.936140	-2.740057	0.000000
C	0.174284	2.212158	0.000000
O	-0.716622	3.050083	0.000000
H	2.135972	-0.011952	0.000000
H	0.328155	-3.548058	0.000000
H	1.934814	-2.894974	0.000000
H	1.252918	2.520220	0.000000

## b-P35 monomer

HF = -563.6612022

C	-1.065355	-0.135935	-0.000010
C	0.200189	0.462288	0.000205
C	1.097970	-0.636271	0.000018
N	-0.853844	-1.487081	0.000034
H	-1.583869	-2.195555	-0.000017
H	0.467424	1.510469	0.000305
N	0.458959	-1.826962	0.000155
C	-2.465527	0.368892	-0.000119
O	-3.426413	-0.411336	-0.000200
N	-2.604139	1.735814	0.000098
H	-3.542445	2.124440	0.000155
H	-1.805943	2.362303	0.000308
N	2.503024	-0.636707	-0.000041
C	3.320058	0.477753	-0.000073
H	2.945313	-1.554989	-0.000051
O	2.935676	1.642653	-0.000103
H	4.393417	0.186989	-0.000117

b-P35<sub>syn</sub> monomer

HF = -563.6428887

C	1.096174	-0.605064	0.000388
C	0.161276	0.422701	-0.000501
C	-1.104628	-0.244896	-0.000285
N	0.380572	-1.781590	0.001120
H	0.732779	-2.734309	0.001886
H	0.398432	1.477713	-0.001459
N	-0.968248	-1.584005	0.000733
C	-2.487244	0.352568	-0.001098
O	-3.516481	-0.319566	-0.002321
N	-2.507918	1.736278	0.001600
H	-3.413679	2.194831	0.002010
H	-1.668443	2.304618	0.004301
N	2.498908	-0.605113	0.000548
C	3.300785	0.531738	-0.000013
H	2.979411	-1.502819	0.001084
O	2.887979	1.682121	-0.001024
H	4.378151	0.258253	-0.000023

## c-P35 monomer

HF = -638.9122575

C	-1.147798	0.283864	-0.000174
C	0.127080	-0.302791	-0.000430
C	1.024109	0.807385	-0.000174
N	-0.939302	1.641657	0.000069
H	-1.675021	2.343596	0.000311
N	0.364568	1.986015	-0.000203
C	-2.526257	-0.258722	-0.000079
O	-3.508934	0.498066	0.000515
N	-2.611704	-1.628617	0.000064
H	-3.535242	-2.050698	0.000459
H	-1.777739	-2.213153	-0.000102
N	2.440540	0.857285	-0.000069

C	3.315799	-0.188208	0.000230
H	2.830627	1.800153	-0.000149
O	3.012753	-1.392195	0.000611
H	4.369996	0.147393	0.000446
H	1.352312	-1.771287	-0.000204
O	0.358526	-1.643315	-0.000628

c-P35<sub>syn</sub> monomer  
HF = -638.8896725

C	1.036922	0.767755	0.000022
C	0.104822	-0.275187	-0.000008
C	-1.174533	0.373645	-0.000016
N	0.293567	1.932742	0.000093
H	0.633228	2.890001	0.000160
O	0.297636	-1.626213	-0.000048
N	-1.042086	1.716859	0.000037
C	-2.553009	-0.235706	-0.000032
O	-3.579902	0.443334	-0.000119
N	-2.563440	-1.614557	0.000069
H	-3.468817	-2.074338	0.000054
H	-1.706955	-2.164852	0.000143
N	2.450726	0.818947	0.000066
C	3.316219	-0.245410	0.000007
H	2.879969	1.743262	0.000197
O	2.989104	-1.438241	-0.000109
H	4.374233	0.079580	0.000045
H	1.279749	-1.793224	-0.000089

a-P35 trimer  
HF = -1184.7843517

C	3.583599	-0.163057	0.000000
C	4.062000	1.160534	0.000000
C	2.899835	1.973482	0.000000
N	1.778886	1.193223	0.000000
N	2.214911	-0.098962	0.000000
H	5.100138	1.474818	0.000000
H	1.509549	-0.872315	0.000000
H	5.473291	-1.196368	0.000000
H	3.651365	3.897368	0.000000
H	0.000000	1.743246	0.000000
C	-1.650918	3.184157	0.000000
C	-3.036462	2.937236	0.000000
C	-3.159901	1.524341	0.000000
N	-1.923951	0.943202	0.000000
N	-1.022556	1.966608	0.000000
H	-3.827443	3.679394	0.000000
H	-1.698792	5.337485	0.000000
H	-5.202065	1.213266	0.000000
H	-1.514600	-0.872120	0.000000
C	-1.932931	-3.023225	0.000000
C	-1.024151	-4.097928	0.000000
C	0.259959	-3.495606	0.000000
N	0.142368	-2.134885	0.000000
N	-1.195048	-1.868821	0.000000

H	-1.268756	-5.154621	0.000000
H	-3.773128	-4.142900	0.000000
H	1.553716	-5.105778	0.000000
N	2.809000	3.339504	0.000000
H	1.897685	3.803832	0.000000
C	4.374367	-1.382216	0.000000
O	3.942775	-2.540602	0.000000
O	-4.170691	-2.144780	0.000000
O	0.229966	4.681927	0.000000
C	-0.989224	4.477988	0.000000
C	-3.384163	-3.098450	0.000000
N	1.489582	-4.097474	0.000000
N	-4.297696	0.762773	0.000000
H	-4.244299	-0.258577	0.000000
H	2.346409	-3.538808	0.000000

a-P35<sub>syn</sub> trimer

HF = -1184.7848652

C	1.968686	-2.950745	0.000000
C	1.116704	-4.065373	0.000000
C	-0.198957	-3.519852	0.000000
N	-0.178841	-2.161069	0.000000
N	1.149028	-1.843252	0.000000
N	3.328858	-2.839893	0.000000
C	-1.425260	-4.311503	0.000000
O	-2.586645	-3.890496	0.000000
H	1.398674	-5.112340	0.000000
H	1.453516	-0.838836	0.000000
H	3.788734	-1.922481	0.000000
H	3.893643	-3.678316	0.000000
H	-1.241277	-5.411837	0.000000
H	-1.452540	-0.837557	0.000000
C	-3.539514	-0.228923	0.000000
C	-4.079406	1.066023	0.000000
C	-2.949529	1.933121	0.000000
N	-1.782671	1.236780	0.000000
N	-2.170638	-0.072326	0.000000
N	-4.123656	-1.462241	0.000000
C	-3.021856	3.390959	0.000000
O	-2.076266	4.185911	0.000000
H	-5.127308	1.344518	0.000000
H	-3.559309	-2.319333	0.000000
H	-5.132180	-1.531697	0.000000
H	-4.066677	3.781943	0.000000
H	0.000000	1.676488	0.000000
C	1.570791	3.179075	0.000000
C	2.962163	2.998958	0.000000
C	3.148054	1.586937	0.000000
N	1.961498	0.924653	0.000000
N	1.021882	1.915328	0.000000

N	0.794743	4.301610	0.000000
C	4.447058	0.921213	0.000000
O	4.663631	-0.294986	0.000000
H	3.727423	3.767079	0.000000
H	-0.229741	4.241443	0.000000
H	1.238696	5.209822	0.000000
H	5.307560	1.631220	0.000000

b-P35 trimer

HF = -1691.0536436

C	1.687606	3.212321	0.015955
C	0.694148	4.199014	0.008465
C	-0.520713	3.477314	-0.007846
N	1.052511	1.998175	0.003917
H	1.458407	1.037820	0.001588
H	0.788892	5.276258	0.012871
N	-0.301560	2.137861	-0.010306
C	3.162035	3.343354	0.031773
O	3.936622	2.368460	0.031289
N	3.638932	4.627084	0.047177
H	4.645146	4.764446	0.057236
H	3.025979	5.435455	0.048212
N	-1.828912	3.960369	-0.020661
C	-2.184142	5.294036	-0.018707
H	-2.590117	3.261741	-0.032634
O	-1.410304	6.250795	-0.005392
H	-3.289224	5.405593	-0.030753
H	-6.456039	1.635564	-0.006488
O	-4.025286	2.222701	-0.048547
N	-5.832267	0.834144	0.004422
C	-4.482297	1.064547	-0.018406
H	-6.224763	-0.101358	0.028869
C	-3.630383	-0.146267	-0.006534
H	-1.634695	0.745842	-0.024459
N	-2.261542	-0.086749	-0.018175
C	-3.985708	-1.500412	0.011088
H	-4.965526	-1.957907	0.020855
N	-1.702790	-1.328405	-0.005897
C	-2.752016	-2.189674	0.010061
O	-4.706551	-4.349719	0.063208
N	-2.515073	-3.563524	0.022875
C	-3.490696	-4.539403	0.047555
H	-1.529256	-3.872427	0.008090
H	-3.033765	-5.551398	0.052424
O	6.120557	-1.901062	-0.007188
C	5.678229	-0.752808	-0.001651
H	6.327390	0.147911	0.005494
N	4.345605	-0.394844	-0.003645
H	4.179066	-3.318202	-0.014576
C	3.292542	-2.698916	-0.014044
C	3.273801	-1.286232	-0.009088
H	3.198322	-5.338447	-0.014430
H	4.120545	0.613529	0.004689
N	2.191615	-5.464513	-0.019250

C	1.941612	-3.067073	-0.017842
C	1.318170	-4.409557	-0.022117
N	2.003395	-0.807417	-0.009558
H	1.807748	-6.404733	-0.022623
N	1.206405	-1.910733	-0.015947
O	0.086536	-4.592183	-0.027808
H	0.171948	-1.783222	-0.015498

b-P35<sub>syn</sub> trimer

HF = -1691.0497477

C	-2.689325	-2.311295	-0.026832
C	-2.197188	-3.616610	-0.040569
C	-0.785091	-3.463868	-0.035969
N	-1.604150	-1.471454	-0.015906
H	-1.620902	-0.424003	-0.002361
H	-2.809552	-4.507760	-0.045640
N	-0.425091	-2.156362	-0.020738
C	0.240274	-4.542538	-0.047020
O	1.468036	-4.343385	0.011221
N	-0.251697	-5.818955	-0.126764
H	0.411330	-6.588232	-0.130751
H	-1.244137	-6.020028	-0.182186
N	-3.981853	-1.806076	-0.020610
C	-5.124461	-2.587134	-0.019733
H	-4.101096	-0.774941	-0.003215
O	-5.154933	-3.815122	-0.031812
H	-6.034112	-1.951955	-0.006351
N	3.551933	-2.542154	0.111661
C	3.345507	-1.170886	0.057939
N	2.076814	-0.648455	0.018725
H	1.176752	-1.183694	0.007299
N	2.084740	0.714287	-0.037604
C	3.397988	1.053006	-0.031113
C	3.824304	2.478041	-0.087219
N	5.178992	2.684058	-0.120735
H	5.848582	1.922244	-0.119850
H	5.517056	3.640897	-0.158811
O	3.039225	3.444676	-0.104277
H	2.718327	-3.160952	0.091949
C	4.798373	-3.142866	0.142838
H	4.701272	-4.248008	0.168800
O	5.878310	-2.557180	0.143295
C	4.232716	-0.094562	0.028892
H	5.310281	-0.181843	0.051845
N	-1.663175	1.445216	0.020508
N	-0.478569	2.120311	-0.003476
H	0.435017	1.608459	-0.021252
C	-0.659620	3.480475	0.000135
N	0.425806	4.344919	-0.024818
H	1.377884	3.931497	-0.051608
C	0.323224	5.725359	-0.019945
H	1.328822	6.193640	-0.047684
O	-0.723254	6.367766	0.010120
C	-2.035443	3.710905	0.028738



H	-2.497882	4.688281	0.034501
C	-2.612780	2.413180	0.040234
C	-4.060419	2.067720	0.065422
N	-4.917447	3.136058	0.109627
H	-4.593032	4.096660	0.130635
H	-5.915713	2.949639	0.119329
O	-4.503804	0.904093	0.046637

c-P35 trimer

HF = -1916.8184387

C	-2.864994	-2.037706	-0.006382
C	-4.061321	-1.266237	0.008170
C	-3.624684	0.071259	0.008246
N	-1.775973	-1.232989	-0.014460
C	-4.407138	1.317517	0.015482
O	-3.880529	2.453635	0.009183
N	-5.763188	1.159808	0.029427
H	-6.338529	1.996618	0.034695
H	-6.189191	0.232757	0.031952
N	-2.671949	-3.432189	-0.012406
C	-3.631727	-4.392624	-0.007089
H	-1.684301	-3.762768	-0.019591
O	-4.867925	-4.214850	0.002800
H	-3.199510	-5.408056	-0.012711
N	-1.637746	4.020053	-0.020115
C	-0.332074	3.494657	-0.006832
N	-0.175578	2.149628	0.005301
C	1.875532	3.104923	0.012944
C	3.346290	3.165907	0.024661
N	3.878784	4.423492	0.018913
H	3.281197	5.250750	0.008742
H	4.890033	4.513175	0.028474
O	4.071855	2.145424	0.039360
H	-2.415690	3.327240	-0.012012
C	-1.995232	5.330131	-0.029293
H	-3.091594	5.458046	-0.034884
O	-1.227394	6.314942	-0.032172
C	0.932026	4.148492	-0.003080
N	1.956654	-0.921754	-0.016182
C	3.198077	-1.461776	-0.009428
N	4.308000	-0.595481	-0.006425
H	4.099696	0.424830	-0.002954
C	5.620256	-0.944984	-0.001918
H	6.281734	-0.061453	0.000981
O	6.085586	-2.103609	-0.001213
C	3.128824	-2.883623	-0.004784
C	1.752208	-3.175227	-0.009345
C	1.065000	-4.477092	-0.004654
N	1.882754	-5.570616	0.006614
H	2.898262	-5.472233	0.009971
H	1.449582	-6.489152	0.010587
O	-0.182207	-4.590644	-0.009864
H	0.359939	5.976621	-0.025252
H	4.996771	-3.309073	-0.000439

H	-5.363976	-2.670965	0.015151
O	-5.361116	-1.655620	0.019417
O	4.116382	-3.814202	0.002854
O	1.239707	5.470095	-0.012569
H	1.508557	0.947888	0.023033
H	-1.571555	0.826411	-0.006930
H	0.071596	-1.774808	-0.022058
N	1.159099	1.927808	0.018749
N	-2.247224	0.035288	-0.005835
N	1.094343	-1.964320	-0.016339

c-P35<sub>syn</sub> trimer

HF = -1916.806871

C	-1.973380	-2.923564	0.000000
C	-1.146910	-4.057792	0.000000
C	0.181400	-3.542419	0.000000
N	-1.138615	-1.834205	0.000000
H	-1.435510	-0.826968	0.000000
N	0.171349	-2.178719	0.000000
C	1.445486	-4.317474	0.000000
O	2.582154	-3.793336	0.000000
N	1.302374	-5.674307	0.000000
H	2.146323	-6.239308	0.000000
H	0.379999	-6.111453	0.000000
N	-3.362576	-2.746518	0.000000
C	-4.297342	-3.736345	0.000000
H	-3.722457	-1.762334	0.000000
O	-4.078449	-4.963737	0.000000
H	-5.324154	-3.331425	0.000000
N	4.063904	-1.539213	0.000000
C	3.520887	-0.248248	0.000000
N	2.159906	-0.071166	0.000000
H	1.436095	-0.832038	0.000000
N	1.802143	1.235322	0.000000
C	2.977554	1.926910	0.000000
C	3.015988	3.409096	0.000000
N	4.262409	3.964073	0.000000
H	5.102517	3.384319	0.000000
H	4.329343	4.977468	0.000000
O	1.993493	4.131072	0.000000
H	3.392156	-2.343363	0.000000
C	5.388864	-1.852191	0.000000
H	5.553124	-2.943648	0.000000
O	6.341364	-1.047695	0.000000
C	4.088794	1.035113	0.000000
N	-1.973980	0.941466	0.000000
N	-1.020417	1.903557	0.000000
H	0.000000	1.656401	0.000000
C	-1.546476	3.171205	0.000000
N	-0.698991	4.286119	0.000000
H	0.333296	4.105751	0.000000
C	-1.089141	5.590434	0.000000
H	-0.225410	6.277586	0.000000
O	-2.261667	6.014178	0.000000

C	-2.942034	3.022695	0.000000
C	-3.159981	1.614738	0.000000
C	-4.463298	0.907705	0.000000
N	-5.566924	1.709966	0.000000
H	-5.484848	2.727386	0.000000
H	-6.478159	1.261442	0.000000
O	-4.577896	-0.338733	0.000000
O	5.398435	1.408835	0.000000
H	5.947347	0.560692	0.000000
O	-1.479184	-5.378604	0.000000
H	-2.488078	-5.428534	0.000000
O	-3.919461	3.971046	0.000000
H	-3.458438	4.870012	0.000000