Electronic Supplementary Information

An Infrared Spectroscopic and Theoretical Study on $(CH_3)_3N$-H^+-$(H_2O)_n$, n = 1 – 22: Highly Polarized Hydrogen Bond Networks of Hydrated Clusters

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Contents

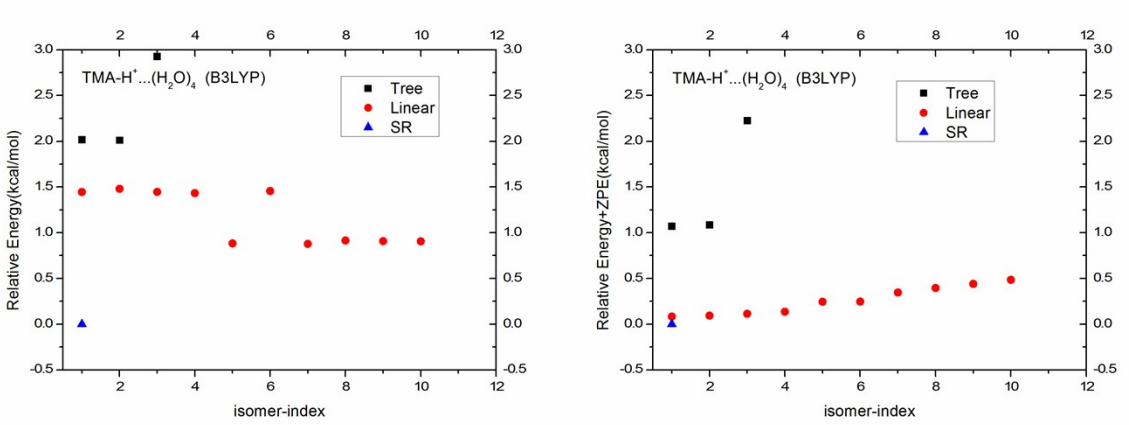
Supplementary Information (I)

Number of stable isomers optimized with B3LYP/6-31+G*.

B3LYP	Tree	Linear	SR	DR	MR	all
n=3	0	2	0	0	0	2
n=4	3	10	1	0	0	14
n=5	11	45	27	2	2	87
n=6	118	97	266	136	21	638

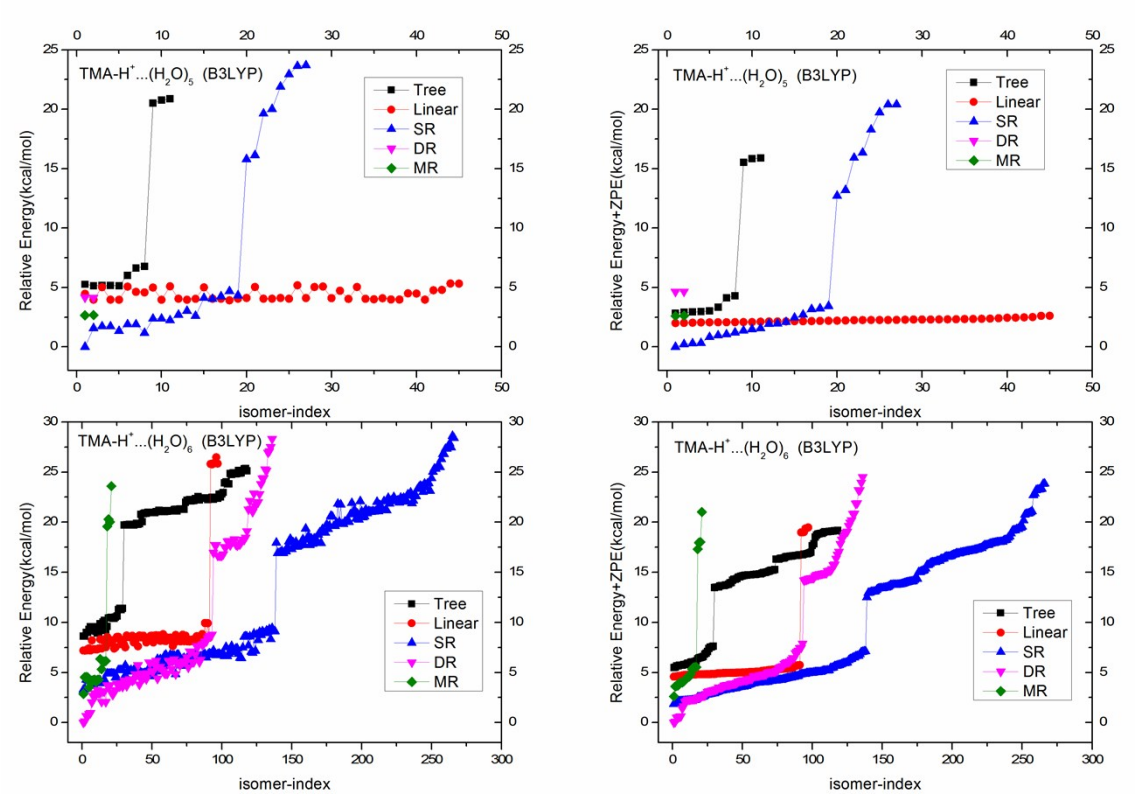
Geometry of all these isomers is available upon request.

Relative energies of TMA-$H^+(H_2O)_4$ with B3LYP/6-31+G*



In all 14 isomers, we can only find protonated TMA. We did not find any stable isomers with a proton transfered to the water moiety.

Relative energies of all isomers TMA-$H^+(H_2O)_5$ (top) and TMA-$H^+(H_2O)_6$ (bottom) with B3LYP/6-31+G*



One can see a clear energy gap between two groups of isomers (regardless of their morphology): the more stable ones have protonated TMA ion cores and those less stable (by at least 12 kcal/mol) have a proton transfered to to the water moiety.

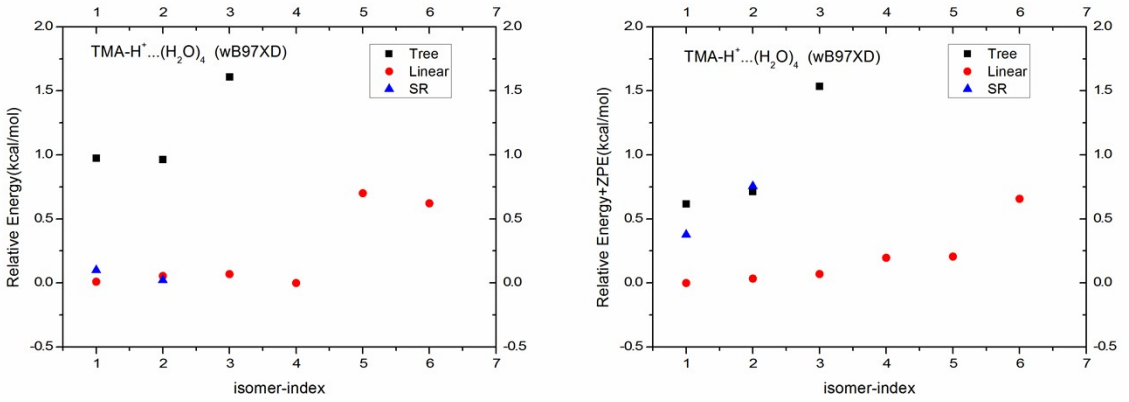
Supplementary Information (II)

Number of stable isomers after re-optimization with ωB97xD /6-311+G(2d,p).

	Tree	Linear	SR	DR	MR	all
n=3	0	2	0	0	0	2
n=4	3	6	2	0	0	11
n=5	10	43	30	2	2	87
n=6	94	57	249	115	32	547

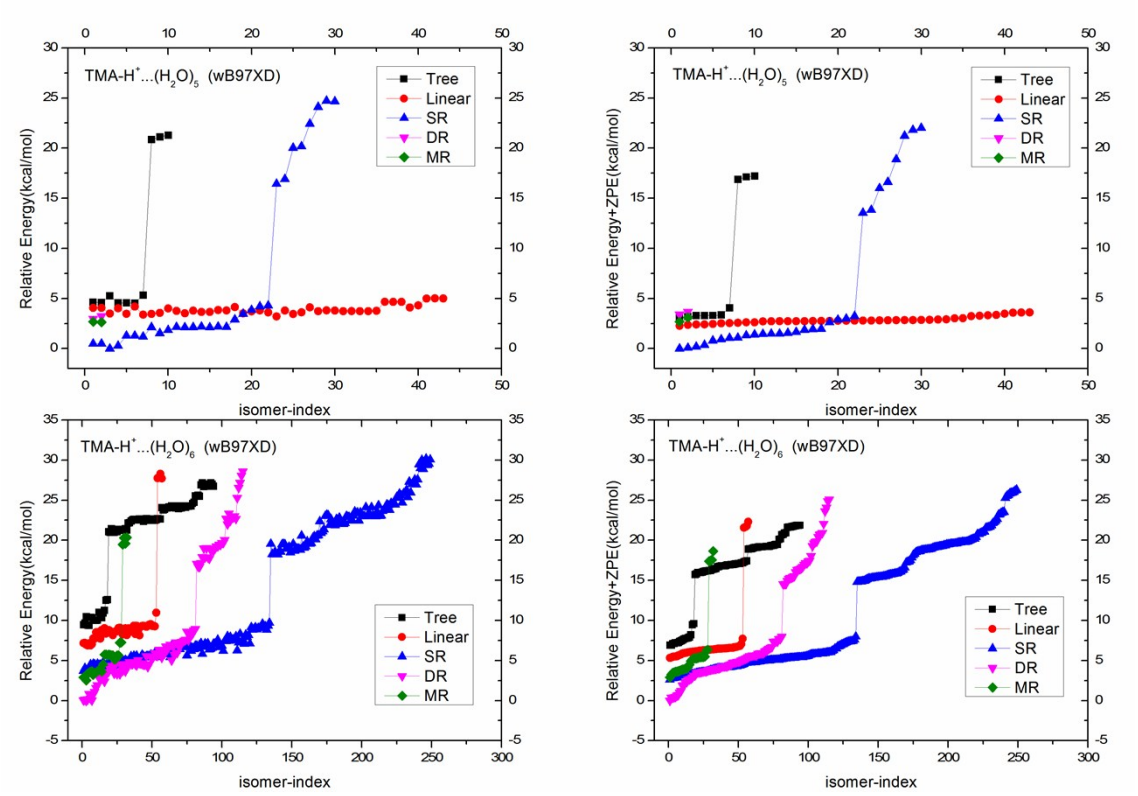
Geometry of all these isomers is available upon request.

Relative energies of TMA-$H^+(H_2O)_4$ with ωB97xD/6-311+G(2d,p)



In all 11 isomers, we can only find protonated TMA. We did not find any stable isomers with a proton transfered to the water moiety.

Relative energy of all isomers TMA-H$^+$(H2O)$_5$ (top) and TMA-H$^+$(H2O)$_6$ (bottom) with ωB97xD/6-311+G(2d,p)

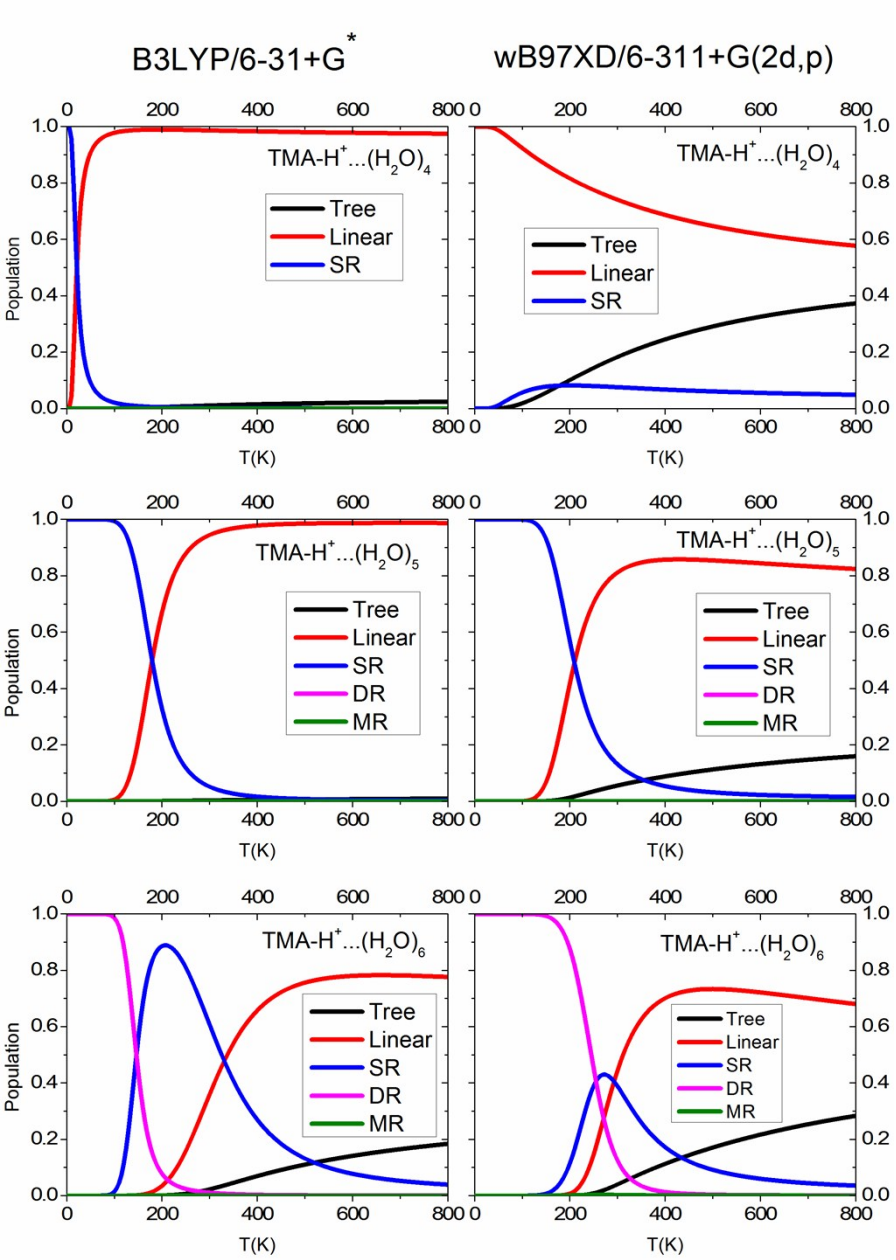


One can see a clear energy gap between two groups of isomers (regardless of their morphology): the more stable ones have protonated TMA ion cores and those less stable (by at least 12 kcal/mol) have a proton transfered to to the water moiety. Note that this result is essentially same as that with the B3LYP calculations.

Supplementary Information (III)

Temperature dependence of isomer populations of TMA-H$^+$(H$_2$O)$_n$ (n = 4 – 6) using B3LYP/6-31+G* (left panels) and ωB97xD/6-311+G(2d,p) (right panels).

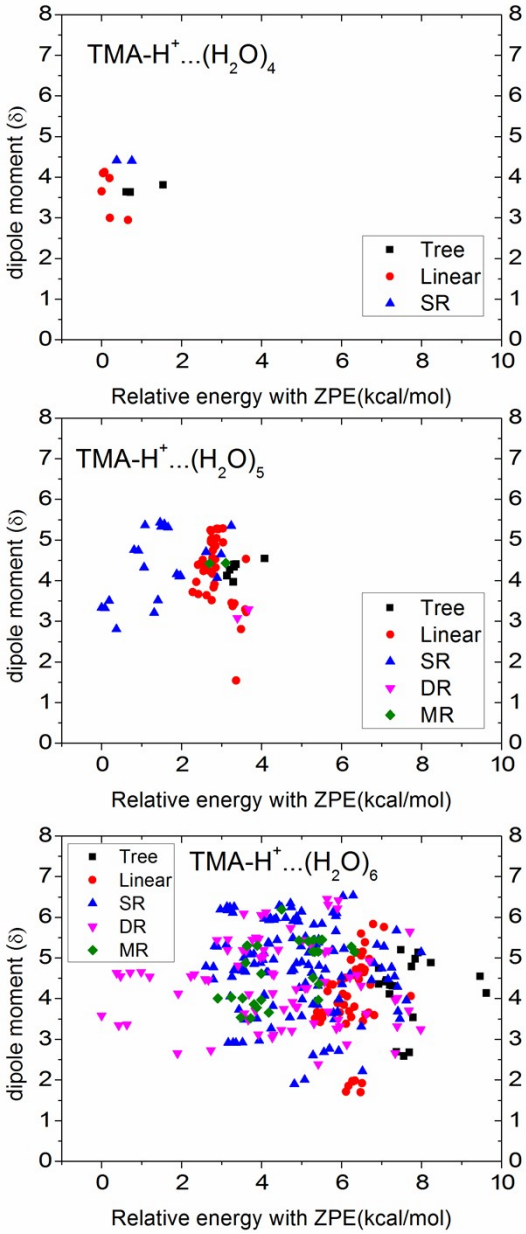
The two functionals give reasonable agreements for n = 5 and 6.



Supplementary Information (IV)

Complete calculation data sets on dependence of the magnitudes of dipole moment on their morphology for TMA-H^+-$(H_2O)_n$ (n = 4 – 6).

All the calculations were performed based on the geometry optimized by ωB97xD/6-311+G(2d,p).



Supplementary Information (V)

XYZ coordinates of all the structures shown in Figures 3 and 6 in the main text.

n=1

1I

N	-0.006459	-0.007645	-0.406322
H	0.024790	-0.019462	0.630633
C	1.399345	0.000067	-0.891293
C	-0.733662	-1.229783	-0.841349
C	-0.729334	1.229099	-0.805488
H	1.899387	-0.900872	-0.541774
H	1.903240	0.880397	-0.497768
H	-0.192383	-2.107336	-0.494042
H	-1.732379	-1.217939	-0.409922
H	-0.191780	2.093410	-0.420800
H	-1.734230	1.200489	-0.388896
H	1.398297	0.025366	-1.980193
H	-0.796303	-1.236775	-1.928698
H	-0.780043	1.275838	-1.892451
O	0.057848	0.006280	2.386758
H	-0.471994	0.557957	2.968285
H	0.603421	-0.537146	2.961500

n=2

2I

O	1.665064	-0.185672	0.402474
O	1.528169	0.227258	3.083227
H	2.556312	-0.381107	0.107883
H	0.243270	-0.122207	-0.456600
H	1.860501	1.028470	3.495944
H	1.645683	-0.473033	3.730065
H	1.698779	-0.052934	1.372024
N	-0.687906	-0.040717	-0.928146
C	-0.438171	0.267735	-2.358785
H	0.128281	1.194292	-2.427072

H 0.129623 -0.547046 -2.803581
H -1.392955 0.377225 -2.871792
C -1.415731 1.061969 -0.250455
H -1.522416 0.819657 0.805069
H -0.844791 1.981666 -0.360127
H -2.397793 1.176540 -0.707999
C -1.384019 -1.341370 -0.760637
H -0.783003 -2.125949 -1.215648
H -1.506636 -1.541460 0.301689
H -2.358478 -1.289381 -1.245012

n=3

3I

O -2.342235 -0.045060 -2.399326
O -2.601357 -0.046749 2.376923
O -1.106930 -0.032086 0.066157
H -1.698147 -0.035175 0.840252
H -3.093794 0.707572 2.708553
H -2.815764 0.709523 -2.757576
H -1.645052 -0.036702 -0.744975
H -2.771197 -0.823045 -2.763659
H 0.481981 0.032515 0.061543
H -3.042756 -0.826309 2.721863
C 2.048181 -0.568211 1.260395
H 1.646801 -1.575455 1.352656
H 3.137005 -0.601635 1.229449
H 1.718573 0.034004 2.104830
C 1.905732 -0.768199 -1.181313
H 1.520834 -1.777769 -1.052422
H 1.457490 -0.317590 -2.064735
H 2.990408 -0.791551 -1.283799
C 1.967921 1.450418 -0.133484
H 1.520382 1.867008 -1.033533
H 1.628732 2.010794 0.735339
H 3.054593 1.494096 -0.204059
N 1.538902 0.038696 0.007483

3II

O -0.630156 1.867765 -0.599039
O -0.093347 0.121793 3.272859
O 1.266073 1.443569 1.270910
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H -0.435980 0.295093 -1.145466
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H 2.001322 1.998838 1.539341
H 0.049484 1.992983 0.092513
N -0.236403 -0.728919 -1.212686
C -0.867358 -1.246420 -2.450943
H -1.940163 -1.070617 -2.402333
H -0.446249 -0.725942 -3.308774
H -0.669989 -2.314685 -2.533875
C -0.821178 -1.346919 0.004893
H -0.369028 -0.894166 0.885671
H -1.893944 -1.164732 0.010078
H -0.624430 -2.418533 -0.012080
C 1.241806 -0.874002 -1.238458
H 1.627996 -0.386104 -2.131316
H 1.648802 -0.394162 -0.349835
H 1.493824 -1.933914 -1.256207

n=4

Linear

H -2.542389 0.535160 -0.264658
O -1.643924 0.859974 -0.191179
H -0.647309 1.868835 -1.073078
C 0.872616 2.983076 -0.280276
H 1.188081 2.178265 0.382813
H 1.738561 3.543745 -0.631485
H 0.189824 3.644924 0.248791
C 1.020703 1.428575 -2.174418

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N 0.166112 2.406178 -1.452828
H -1.065165 0.121652 0.091632
O 0.465663 -0.691582 0.377335
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H 0.549478 -1.644459 0.445230
O 1.758969 0.754981 2.258491
H 2.698230 0.582206 2.463616
H 1.328252 0.908750 3.102223
O 4.411777 0.249714 2.797742
H 4.751249 -0.583319 3.132339
H 5.064005 0.916272 3.024268

Tree

H -2.677088 0.967995 0.299643
O -1.841881 0.847149 -0.153982
H -0.848025 1.828914 -1.051997
C 0.902184 2.760527 -0.541460
H 1.147398 1.950448 0.144021
H 1.797157 3.139167 -1.034426
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C 0.578281 1.106416 -2.323705
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H 2.075196 -2.456296 -0.709512
H 0.604904 -2.754721 -1.015826
O 0.660725 -0.578981 3.779768
H 0.097842 -1.104456 4.351968
H 1.390766 -0.275315 4.323032

SR

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O -1.368145 0.758899 -0.328147
H -0.564976 1.879969 -1.075107
C 0.450483 3.623543 -0.638943
H 1.084310 3.127751 0.093783
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H -0.411194 4.060414 -0.137827
C 1.106811 1.926334 -2.282562
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H 1.726230 1.454750 -1.521792
C -0.955602 3.211635 -2.607685
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H -1.319702 2.424583 -3.264876
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O -1.629558 -0.474050 3.644118
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H -2.149708 -1.194336 4.012649
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H -2.594788 0.822853 2.555226

n=5

Linear

O -1.240567 -2.027566 0.604800
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H -2.759882 -4.310785 -1.496145
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H 3.261187 1.781415 -0.542951
H -0.883269 1.155280 0.450794
H -1.367399 -1.171493 0.157732
N -1.811176 -1.391519 3.109930
C -2.067503 -2.545648 4.000326
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H -2.941835 -3.084575 3.640399
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C -2.980962 -0.483690 3.025774
H -3.855481 -1.062595 2.734248
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H -0.399925 0.142461 2.778759
H 0.256349 -1.352317 3.485883
H -0.711252 -0.243408 4.495917

Tree

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O -2.060782 0.177909 -0.721047
O 0.990811 2.787316 0.768245
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H -3.094974 -1.819794 -3.193209
H -3.012898 -2.863293 -2.071605
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C -2.534998 2.744831 1.237506
H -2.743872 3.248019 0.295383
H -1.466013 2.555244 1.317174
H -2.872674 3.360148 2.071694

SR

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O 1.463062 3.500410 1.352899
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H 0.590874 -1.436884 -0.741405
H -1.474602 -2.796054 -0.884364
H 2.088312 -1.384844 -0.308564
N -0.700856 1.746193 -2.530466
C -0.397915 0.440488 -3.173714
H 0.672178 0.256229 -3.100988
H -0.931518 -0.349511 -2.647051
H -0.708719 0.482984 -4.217300
C -2.163093 1.992768 -2.455724
H -2.616887 1.206679 -1.855199
H -2.333323 2.957484 -1.981255
H -2.575155 1.997250 -3.464361
C 0.014788 2.860979 -3.195616
H -0.173434 3.782865 -2.648549
H 1.081363 2.644914 -3.198356
H -0.346491 2.957208 -4.218953

DR

O 0.500613 0.272317 1.466410
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O -1.980741 -0.062412 0.417324
O 1.625787 1.349072 -0.896090
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H 0.258756 -1.288563 -1.249542
H 1.583210 2.245963 -1.236106

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H -1.715601 -0.150790 -0.507893
H -0.352654 -0.948847 -2.640564
H 0.978327 0.828261 -1.405419
H -2.875030 0.282501 0.433745
H 0.896178 -2.706786 0.664601
N 3.907326 -1.126615 0.394774
C 4.742875 -2.235172 0.918649
H 4.708470 -3.067954 0.218862
H 4.352441 -2.546336 1.885760
H 5.768805 -1.886101 1.028859
C 3.855937 0.017804 1.343223
H 3.409710 -0.316367 2.277662
H 3.245016 0.801083 0.901516
H 4.869608 0.378295 1.514822
C 4.344379 -0.689350 -0.956143
H 3.652017 0.074614 -1.306320
H 4.335201 -1.547167 -1.626059
H 5.353536 -0.284631 -0.885710

MR

O -0.308869 -1.334204 1.298950
O 1.717279 -1.415942 -0.821159
O -2.099917 0.031114 -0.142567
O 1.694308 0.684254 0.982623
O 0.254637 0.858444 -1.459795
H 2.201604 -0.875208 -0.178682
H 0.195229 -1.860679 0.665578
H -1.492264 -0.500646 0.424579
H 0.717406 0.005219 -1.551521
H 2.205010 1.315543 1.493637
H 0.323545 -0.652735 1.572300
H -1.511596 0.475059 -0.771987
H 0.434430 1.357775 -2.259534
H 1.240399 1.175517 0.280606
H -3.666296 -0.125520 0.041355

H 2.354134 -1.992511 -1.249112
N -4.678844 -0.314713 0.286390
C -5.362434 -0.767828 -0.947571
H -5.301350 0.019500 -1.696310
H -4.866372 -1.662693 -1.317858
H -6.406717 -0.985679 -0.724484
C -4.662133 -1.374235 1.324551
H -4.180809 -2.260277 0.915666
H -4.096754 -1.017437 2.183161
H -5.685058 -1.606382 1.619899
C -5.255415 0.948692 0.804060
H -4.685478 1.264603 1.675334
H -5.191258 1.710676 0.029915
H -6.297415 0.784361 1.077660

n=6

Linear

O -2.809938 -1.980821 0.208506
O 2.014219 1.523014 1.825961
O -0.024961 2.378487 0.173601
O -4.511162 -4.099467 -0.404845
O -0.523246 -1.880243 -1.206765
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H -1.943382 -2.050240 -0.247966
H -0.394080 -0.959837 -1.505468
H -4.754330 -4.707060 0.298009
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H -3.321771 -2.779668 -0.007701
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H 0.331858 -2.206486 -0.922463
H -0.036910 1.030901 -2.762769
H 0.693051 2.096498 0.771932

N -4.006556 0.318386 -0.284363
C -3.356916 1.344355 0.563478
H -2.305534 1.429021 0.292958
H -3.443396 1.043115 1.605849
H -3.855391 2.302435 0.412812
C -5.426186 0.117980 0.083171
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H -5.834817 -0.693873 -0.515834
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C -3.847667 0.617787 -1.727151
H -4.282337 -0.198041 -2.302231
H -2.785029 0.707789 -1.952099
H -4.364276 1.549786 -1.958503

Tree

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