Electron attachment to microhydrated 4-nitro- and 4-bromo-thiophenol

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Supplementary Information

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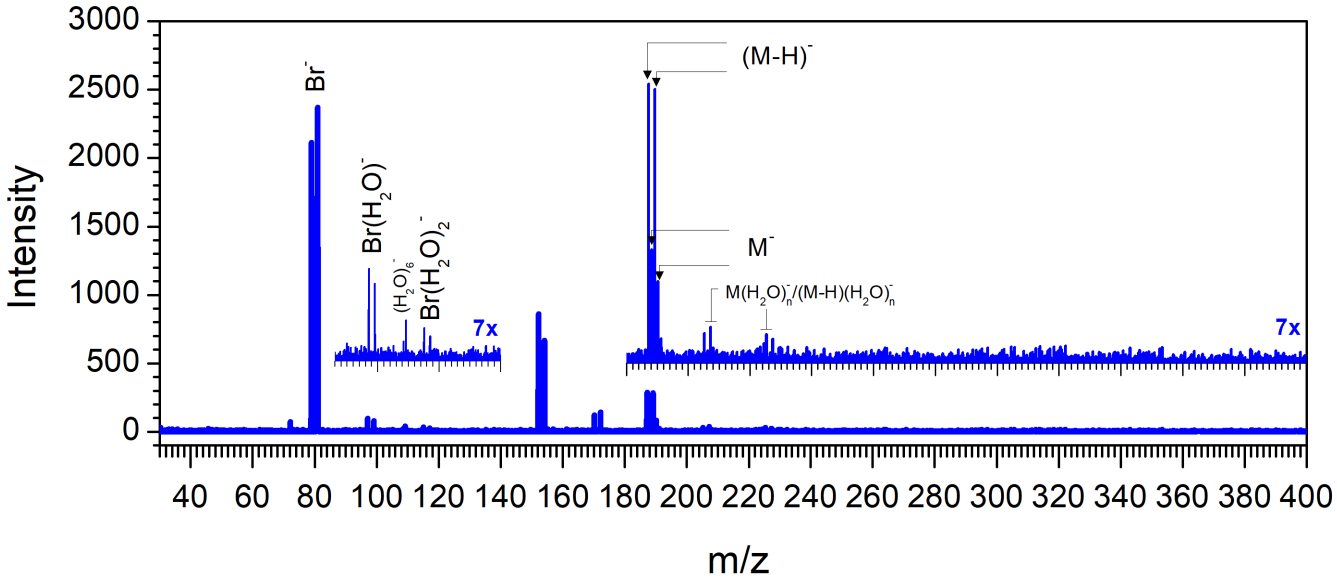

Figure S1 Cumulative negative ion mass spectra (0.6-8.6 eV) of BTP in low hydration conditions (He carrier gas, P_0 = 1.5 bar).

Table 1 Calculated reaction energies for selected anion formation and fragmentation channels, where M stands for BTP or NTP molecule. The calculations were done using B3LYP functional with aug-cc-pVDZ basis set and D3BJ dispersion correction. All energies are presented in units of eV.

row	precursor n=	$BTP(H_2O)_n$ 1	2	3	$NTP(H_2O)_n$ 1	2	3
1	$M(H_2O)_n + e^- \rightarrow [M(H_2O)_n\text{-}H]^- + H$	0.57	0.51	0.5	0.13	0.21	0.21
2	$BTP(H_2O)_n + e^- \rightarrow (BTP(H_2O)_n\text{-}Br) + Br^-$	0.02	0.00	0.07	-	-	-
3	$BTP(H_2O)_n + e^- \rightarrow (BTP\text{-}Br) + Br(H_2O)_n^-$	-0.34	-0.53	-0.26	-	-	-
4	$NTP(H_2O)_n + e^- \rightarrow (NTP(H_2O)_n\text{-}NO_2) + NO_2^-$	-	-	-	1.07	1.02	1.05
5	$M(H_2O)_n \rightarrow M + (H_2O)_n$	0.19	0.39	0.40	0.26	0.43	0.39
6	$M(H_2O)_n \rightarrow M + n(H_2O)$	-	0.62	1.13	-	0.66	1.12
7	$M(H_2O)_n^- \rightarrow M^- + (H_2O)_n$	0.54	0.92	0.96	0.72	0.88	1.17
8	$M(H_2O)_n^- \rightarrow M^- + n(H_2O)$	-	1.15	1.69	-	1.11	1.90

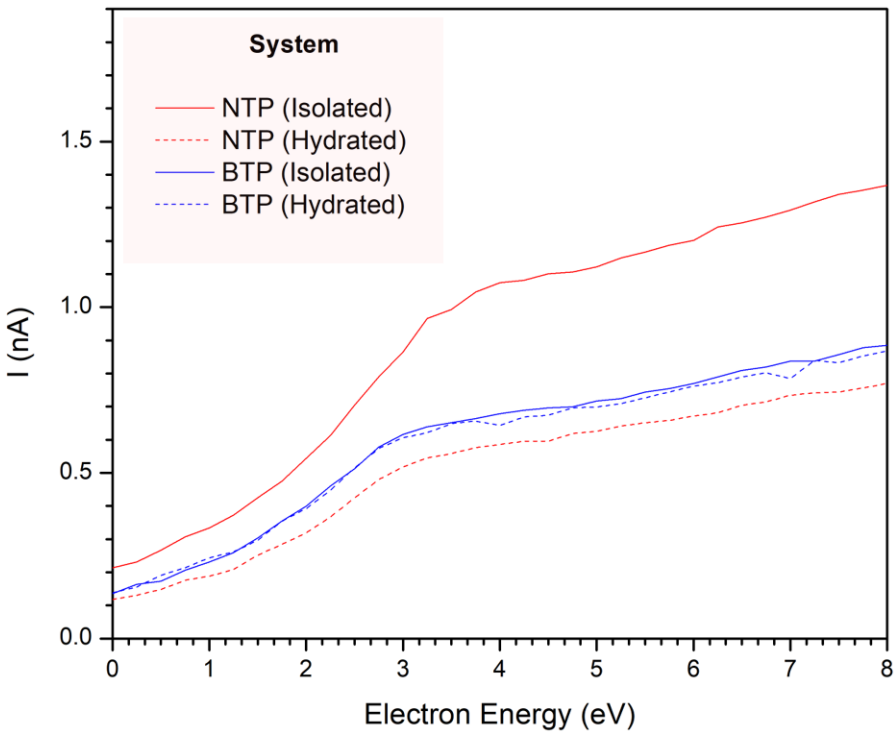

Figure S2 Electron current profiles during the anion mass spectrum measurement of isolated and hydrated NTP and BTP.

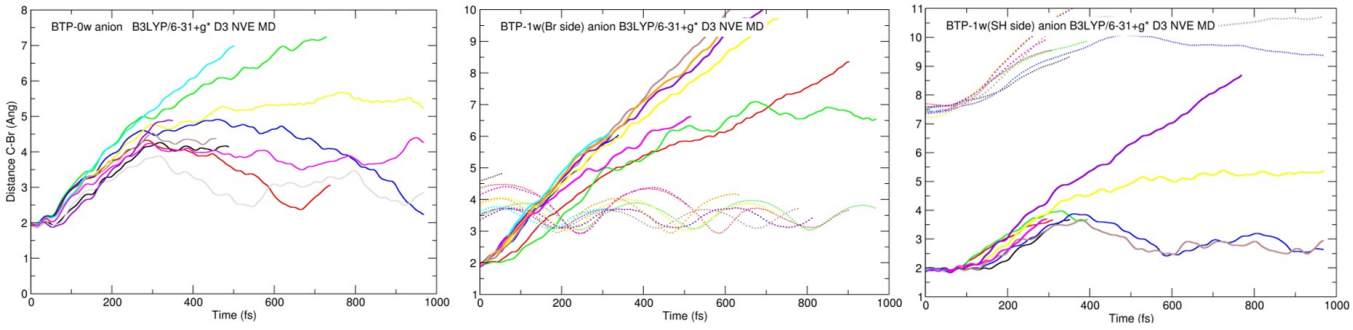

Figure S3 Results of MD simulations at B3LYP/aug-cc-pVDZ level of theory of time evolution of 10 trajectories of BTP and 20 trajectories of BTP(H_2O) clusters upon vertical electron attachment simulated for 1 ps. Figure shows time evolution of distance between Br and nearest C atom (full lines) and Br to H_2O distance (dotted lines) along the simulation. For pure BTP clusters (left panel) we observe C-Br dissociation within 100 fs in all calculations. For BTP(H_2O)$^-$ clusters with H_2O attached to Br atom (left panel) we observe fast dissociation (within 100 fs) of the C-Br bond. The H_2O molecule remains bound to the bromine atom. For BTP(H_2O)$^-$ clusters with H_2O attached to SH group (right panel) we observe either direct dissociation or stabilization of the C-Br bond at distance of ionic bond. In all cases, H_2O remained bound to the SH group.

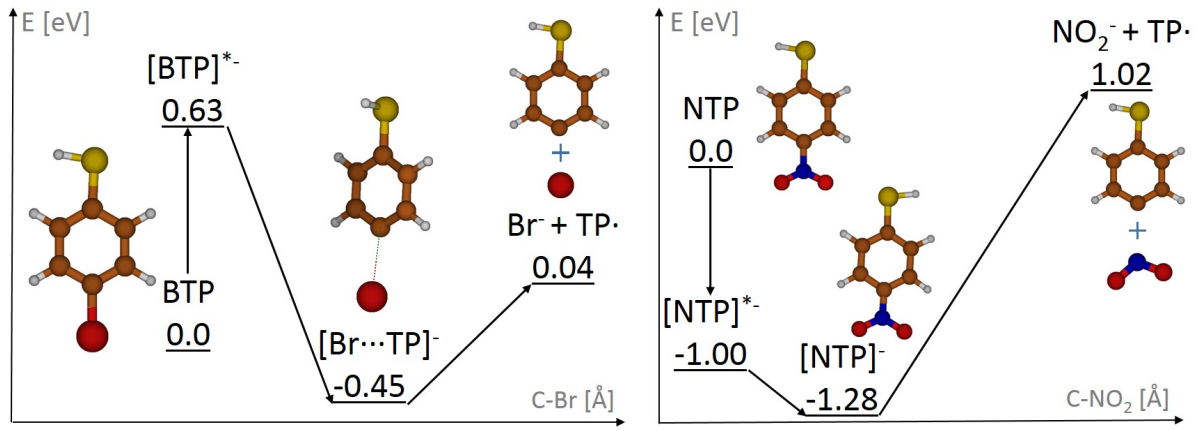

Figure S4 Relative energies of BTP (left) and NTP (right) molecules upon vertical electron attachment and subsequent relaxation to stable anion. Energies calculated at the B3LYP/aug-cc-pVDZ level of theory are presented in eV units.

XYZ coordinates of optimized structures at the LC-ωPBE/aug-cc-pVDZ level of theory used for the energetics calculations:

Bromothiophenol neutral
C 1.348235 1.201033 0.000009
C 2.049569 -0.001389 0.000012
C 1.345629 -1.203843 0.000008
C -0.041010 -1.206170 -0.000001
C -0.726760 0.000046 -0.000004
C -0.039319 1.204485 0.000001
S 3.815949 -0.079691 0.000022
Br -2.608688 0.001831 -0.000017
H 4.038426 1.247717 0.000049
H 1.883586 -2.151609 0.000013
H -0.588266 -2.147073 -0.000005
H 1.882145 2.150658 0.000013
H -0.585058 2.146313 -0.000001

Bromothiophenol anion
C 0.414333 -0.000065 -0.154374
C -0.261332 -1.205913 -0.125275
C -1.653295 -1.208100 -0.065553
C -2.348109 0.000016 -0.028112
C -1.653222 1.208093 -0.065548
C -0.261259 1.205824 -0.125249
S -4.135145 0.000060 0.029494
Br 3.109980 0.000010 0.055076
H -4.273877 -0.000346 1.371821
H -2.211556 2.145530 -0.045398
H 0.293787 2.145607 -0.147946
H -2.211685 -2.145504 -0.045391
H 0.293654 -2.145732 -0.147980

Nitrothiophenol neutral
C -1.211875 0.440148 0.000000
C 0.000000 1.111313 0.000000

C 1.210350 0.438862 0.000000
C 1.206930 -0.945467 0.000000
C -0.000810 -1.643602 0.000000
C -1.208839 -0.943444 0.000000
N 0.001689 2.577454 0.000000
O 1.077754 3.139826 0.000000
S -0.079512 -3.403815 0.000000
O -1.072947 3.142206 0.000000
H 1.248092 -3.626728 0.000000
H -2.153458 -1.485934 0.000000
H -2.139799 1.006825 0.000000
H 2.153744 -1.483242 0.000000
H 2.138791 1.004809 0.000000

Nitrothiophenol anion
C -1.217625 0.446202 0.000000
C 0.000000 1.161189 0.000000
C 1.213293 0.439496 0.000000
C 1.200091 -0.941735 0.000000
C -0.007507 -1.648266 0.000000
C -1.211867 -0.935073 0.000000
N 0.005034 2.541165 0.000000
O 1.121136 3.151416 0.000000
S -0.078041 -3.426650 0.000000
O -1.106222 3.159639 0.000000
H 1.249749 -3.645743 0.000000
H -2.160862 -1.474605 0.000000
H -2.142745 1.016973 0.000000
H 2.148117 -1.483003 0.000000
H 2.141538 1.005310 0.000000

Thiphenolyl radical
C -0.252120 1.209454 -0.000002
C 0.438162 -0.001222 0.000003
C -0.260859 -1.208419 0.000000
C -1.654187 -1.214421 -0.000010
C -2.281093 0.006902 -0.000014
C -1.646299 1.223445 -0.000009
S 2.207838 -0.084341 0.000010
H 2.434667 1.242150 0.000057
H 0.284152 -2.152994 0.000006
H -2.206698 -2.153414 -0.000014
H 0.293549 2.153229 0.000000
H -2.192710 2.166054 -0.000012

BTP(H_2O) neutral
C 0.745464 -1.403440 -0.096701
C -0.613821 -1.683535 -0.089335
C -1.541642 -0.652515 0.017666
C -1.111073 0.667889 0.105189
C 0.247237 0.954283 0.103531

C 1.162784 -0.083846 0.003211
S -3.286099 -1.042556 -0.009218
Br 3.003429 0.305551 -0.004111
O -4.081732 2.229685 -0.080765
H -3.474161 -1.033035 1.326813
H -1.834855 1.479492 0.169927
H 0.592219 1.983857 0.175002
H -0.958347 -2.713714 -0.166732
H 1.475977 -2.205899 -0.179054
H -4.121482 1.270504 -0.205845
H -4.901626 2.574923 -0.443980

BTP(H_2O) anion
C 0.239875 -1.157280 -0.789475
C -1.114159 -1.429563 -0.598401
C -1.891406 -0.560617 0.162207
C -1.319262 0.574837 0.737718
C 0.038476 0.826170 0.560051
C 0.801528 -0.035163 -0.209316
S -3.638688 -0.897205 0.341647
Br 3.443924 0.137850 0.041770
O -3.776716 2.322450 -0.796216
H -3.685474 -0.905227 1.688686
H -1.938922 1.257286 1.322268
H 0.502701 1.697922 1.025030
H -1.573119 -2.319502 -1.032137
H 0.857020 -1.833718 -1.383711
H -3.975329 1.447683 -0.435181
H -2.821787 2.296182 -0.920236

BTP($H_2O)_2$ neutral
C 1.528058 -0.911437 0.043323
C 0.733349 -1.221529 -1.054549
C -0.621524 -0.921851 -1.042386
C -1.177510 -0.326138 0.081063
C -0.393551 -0.016558 1.185560
C 0.963653 -0.299969 1.159072
Br -3.013827 0.077167 0.105762
S 3.270363 -1.248276 -0.058939
O 0.941052 2.403394 -1.221797
O 3.244591 2.025914 0.534317
H 3.462518 -1.508528 1.249115
H 1.172353 -1.698649 -1.929613
H -1.244315 -1.155235 -1.903661
H 1.585768 -0.021152 2.008223
H -0.838609 0.460004 2.056792
H 0.223712 1.851008 -0.897923
H 1.648467 2.303988 -0.565426
H 3.538197 1.151124 0.237775
H 3.930034 2.639460 0.253394

BTP(H_2O)$_2$ anion

C -0.766411 1.136295 1.152534
C -1.527554 1.172738 -0.067654
C -0.875619 0.713082 -1.252168
C 0.454158 0.371933 -1.260577
C 1.224744 0.496859 -0.066551
C 0.565657 0.803907 1.150551
S -3.247728 1.492289 -0.040536
Br 2.981815 -0.196169 -0.024844
O -0.847877 -2.127524 0.421522
O -3.500920 -2.918182 -0.027376
H -3.779477 0.254233 0.206380
H -1.450589 0.644148 -2.176830
H 0.930962 0.044249 -2.184309
H -1.254399 1.406466 2.089835
H 1.123301 0.782591 2.087258
H -2.553376 -2.743687 0.143799
H -3.800849 -2.099079 -0.431123
H -0.774489 -1.406753 1.067794
H -0.500447 -1.696121 -0.374682

BTP(H_2O)$_3$ neutral

C 0.541565 -0.027644 1.130337
C 1.433915 0.364615 0.139729
C 1.003153 1.122904 -0.942004
C -0.334843 1.482532 -1.031541
C -1.240157 1.093852 -0.045328
C -0.793673 0.336909 1.037083
Br 3.240094 -0.155667 0.252618
S -2.930121 1.581882 -0.218312
O -3.593610 -1.112222 1.698883
H -3.417517 0.788642 0.766680
H -1.496388 0.011992 1.802493
H 0.887314 -0.624060 1.972587
H -0.676340 2.067092 -1.885310
H 1.707058 1.423958 -1.715501
H -4.388104 -1.555068 2.006975
H -3.384752 -1.506624 0.824229
O -2.979836 -1.796340 -0.885968
H -3.173457 -0.937138 -1.279720
H -2.045198 -1.964791 -1.109867
O -0.259404 -2.053109 -1.559088
H 0.263551 -2.819003 -1.304327
H 0.205501 -1.292382 -1.187156

BTP(H_2O)$_3$ anion

C -0.464475 -1.129197 -0.482369
C 0.240852 -0.362170 -1.386946
C 1.620603 -0.251894 -1.233395
C 2.253435 -0.893582 -0.169956
C 1.514099 -1.661850 0.732137

C 0.133349 -1.781183 0.575579
S 4.018079 -0.725592 0.058436
Br -3.167617 -0.473999 -0.03787
O 0.998566 1.628498 1.573289
O 1.287175 3.095026 -0.799918
O -1.445243 2.197781 0.541138
H 3.998365 0.520577 0.575569
H 2.025813 -2.142359 1.566546
H -0.465121 -2.354234 1.284029
H 2.207177 0.358847 -1.918789
H -0.270217 0.159491 -2.196397
H -2.015575 1.402353 0.410430
H -1.044836 2.349094 -0.323120
H 1.136439 3.987428 -0.477248
H 1.311108 2.552207 0.016182
H 1.143349 0.704433 1.337059
H 0.039652 1.770396 1.389931

$NTP(H_2O)_1$ neutral
C -1.189445 0.247775 0.000000
C 0.000000 0.955410 0.000000
C 1.221866 0.279381 0.000000
C 1.234470 -1.119278 0.000000
C 0.050194 -1.832604 0.000000
C -1.148343 -1.135491 0.00000
S 2.760617 1.130246 0.000000
N -2.405612 -1.880892 0.00000
O -3.438438 -1.240378 0.00000
O -2.347590 -3.094060 0.00000
O 1.570161 4.363034 0.000000
H 2.249054 2.383092 0.000000
H 2.186587 -1.647647 0.000000
H 0.032295 -2.920111 0.000000
H -0.009372 2.044166 0.000000
H -2.155239 0.750704 0.000000
H 0.769254 4.894174 0.000000
H 2.311319 4.977983 0.000000

$NTP(H_2O)_1$ anion
C -0.871335 -0.287405 0.000000
C 0.000000 0.818227 0.000000
C 1.368169 0.617218 0.000000
C 1.907446 -0.671735 0.000000
C 1.042344 -1.769440 0.000000
C -0.327730 -1.587380 0.000000
S 3.659311 -0.978963 0.000000
N -2.244751 -0.122125 0.000000
O -2.991207 -1.143276 0.000000
O -2.741554 1.059938 0.000000
O -2.070864 3.655592 0.000000
H 4.052609 0.308104 0.000000

H 1.449076 -2.782107 0.000000
H -1.016875 -2.427630 0.000000
H 2.028873 1.485480 0.000000
H -0.402229 1.826841 0.000000
H -2.318129 2.698645 0.000000
H -2.913406 4.113999 0.000000

NTP(H_2O)$_2$ neutral
C 1.511550 -1.306304 0.278431
C 1.837211 -0.007738 -0.077635
C 0.889352 0.884335 -0.551027
C -0.426421 0.468078 -0.669971
C -0.776087 -0.835988 -0.315712
C 0.196101 -1.719026 0.158116
N 3.229473 0.435815 0.051271
O 3.488146 1.580267 -0.260683
S -2.437112 -1.424841 -0.429212
O 4.041413 -0.367092 0.464112
O -2.823258 0.949066 1.935076
O -3.449763 1.785100 -0.659203
H -2.984833 -0.276950 -0.897126
H -0.078666 -2.737279 0.431037
H 2.287584 -1.974791 0.643151
H -1.185854 1.157679 -1.035452
H 1.190197 1.893676 -0.821613
H -3.333029 1.699710 0.305593
H -4.254135 2.292745 -0.792911
H -1.948748 1.185913 2.259969
H -2.747569 0.027188 1.648217

NTP(H_2O)$_2$ anion
C 0.809613 1.187368 0.245362
C 0.124370 -0.043587 0.242578
C 0.846271 -1.240913 0.068243
C 2.215546 -1.196678 -0.104825
C 2.899448 0.024301 -0.115755
C 2.179128 1.209788 0.069421
N -1.244973 -0.076917 0.412947
O -1.846098 -1.203072 0.405852
S 4.667973 0.066427 -0.322184
O -1.875904 1.025275 0.572293
O -4.376791 -0.084171 0.760002
O -6.009762 0.208465 -1.423721
H 4.702637 0.144592 -1.670317
H 2.712197 2.160722 0.072622
H 0.232575 2.097005 0.388593
H 2.777029 -2.121834 -0.236344
H 0.296998 -2.178588 0.076950
H -5.466138 0.098848 -0.607911
H -5.350275 0.309747 -2.114592
H -3.674048 0.599357 0.755314

H -3.781544 -0.847905 0.654441

NTP$(H_2O)_3$ neutral

C 0.130551 -1.817161 0.643291
C 0.885565 -1.041562 -0.222334
C 0.307591 -0.113478 -1.072109
C -1.065525 0.046736 -1.051705
C -1.843334 -0.707911 -0.175893
C -1.239970 -1.642304 0.668038
N 2.336673 -1.203752 -0.226215
S -3.592612 -0.529994 -0.078625
O -0.313343 3.151464 -0.656053
O 2.173658 2.227929 0.428991
O -0.179929 1.738968 1.733204
H -3.701967 0.473330 -0.969282
H -1.847899 -2.230023 1.354442
H 0.623008 -2.537281 1.292006
H -1.522525 0.784717 -1.707180
H 0.926905 0.475744 -1.742982
H -0.237070 2.037562 2.644335
H 0.769079 1.777993 1.489441
H 2.615103 1.515762 -0.053698
H 1.570719 2.648762 -0.206610
H -0.521136 4.086026 -0.571355
H -0.532457 2.750033 0.208656
O 2.805729 -2.173324 0.326399
O 3.005641 -0.347835 -0.786540

NTP$(H_2O)_3$ anion

C -1.111565 -1.214928 -0.053251
C -0.407995 -0.000192 0.019364
C -1.112644 1.213330 0.100157
C -2.494548 1.202165 0.100301
C -3.200642 -0.001326 0.016990
C -2.493393 -1.205219 -0.050625
N 0.974783 0.000714 0.014949
S -4.982735 -0.002959 0.041837
O 3.512292 -0.144099 1.803773
O 3.465830 0.144017 -1.826044
O 5.779635 0.000455 -0.040794
H -5.187080 0.060265 -1.291366
H -3.044305 -2.144173 -0.102549
H -0.542556 -2.139047 -0.108131
H -3.046388 2.139772 0.164964
H -0.544513 2.137566 0.161754
H 3.032907 -0.827221 1.302609
H 3.062499 0.639632 1.446500
H 5.176051 -0.064438 0.718473
H 5.157514 0.063650 -0.785076
H 3.002527 0.831761 -1.316487
H 3.024130 -0.636357 -1.451100

O 1.604887 -1.114762 -0.062226
O 1.604132 1.116632 0.086387