Supplementary Material for Theoretical Study on the Effect of Intramolecular Hydrogen Bonding on OH Stretching Overtone Decay Lifetime of Ethylene Glycol, 1-3 Propanediol, and 1-4 Butanediol

Kaito Takahashi

Institute of Atomic and Molecular Sciences, Academia Sinica,
P. O. Box 23-166, Taipei,10617, Taiwan R.O.C.

Kaito Takahashi

Tel: +886-2-2366-8237
Fax: +886-2-2366-0200
Email: kt@gate.siniaca.edu.tw

Tables for Supplementary Material

Table S1: The optimized OHb bond length, in Angstrom, for BD by M06 and M062X methods using different basis sets along with the results previously reported using QCISD/6-311++G(2d,dp) in ref 13

Method	Basis	ROHb
M06	6-31+G(d,p)	0.9713
M06	6-311+G(2d,p)	0.9673
M06	6-311+G(2df,2p)	0.9660
M06	6-311++G(3df,3pd)	0.9667
M06	aug-cc-PVTZ	0.9668
M06	maug-cc-PV(T+D)Z	0.9669
M062X	6-31+G(d,p)	0.9688
M062X	6-311+G(2d,p)	0.9673
M062X	6-311+G(2df,2p)	0.9639
M062X	6-311++G(3df,3pd)	0.9645
M062X	aug-cc-PVTZ	0.9668
M062X	maug-cc-PV(T+D)Z	0.9655
QCISD	6-311++(2d,2p)	0.9616

From the comparison of calculated length versus the QCISD results from Ref 13, we selected M062X/6-311+G(2df,2p) as the method to use for the present study for different alkane diols.

Table S2 ： The optimized hydrogen bonding distance H…O, in angstrom, and OH…O angle, in degree, for the lowest energy conformers of EG, PD, BD

	MP2/6-311++G(3df,3pd)		M062X/6-311+G(2df,2p)		MPw1PW91/6-311+G(2d,p)	
	RH…O	AOH…O	RH…O	AOH…O	RH…O	AOH…O
EG 1	2.33	108	2.33	107	2.34	108
PD 1	2.00	139	2.03	136	2.02	139
BD 1	1.84	156	1.90	151	1.85	157

Table S3: The calculated integrated absorption coefficient, in km mol^{-1}, for OH_b and OH_f transitions for the two stable conformers for ethylene glycol, propane diol and butane diol, calculated using the B3LYP/6-31+G(d,p) method with the local mode

approximation. The two columns in the right hand side give the ratio between the OH_b versus OH_f intensities.

			Ethylene Glycol			
$\Delta\nu_{OH}$	1b	1f	2b	2f	1b/1f	2b/2f
1	30.90	24.83	32.85	17.41	1.24	1.89
2	2.74	4.10	2.67	3.30	0.67	0.81
3	1.89E-01	2.76E-01	1.90E-01	2.39E-01	0.69	0.80
4	1.64E-02	2.22E-02	1.65E-02	1.99E-02	0.74	0.83
5	1.94E-03	2.38E-03	1.86E-03	2.19E-03	0.81	0.85
			Proponediol			
$\Delta\nu_{OH}$	1b	1f	2b	2f	1b/1f	2b/2f
1	125.53	22.12	116.72	23.24	5.68	5.02
2	1.58	4.34	1.56	3.29	0.37	0.48
3	1.37E-01	2.87E-01	1.40E-01	2.27E-01	0.48	0.62
4	1.51E-02	2.25E-02	1.59E-02	1.86E-02	0.67	0.86
5	1.90E-03	2.38E-03	2.05E-03	2.03E-03	0.80	1.01
			Butanediol			
$\Delta\nu_{OH}$	1b	1f	2b	2f	1b/1f	2b/2f
1	351.99	27.12	341.74	21.29	12.98	16.05
2	0.70	4.35	0.76	3.18	0.16	0.24
3	7.52E-02	2.78E-01	8.61E-02	4.20E-01	0.27	0.21
4	1.40E-02	2.16E-02	1.58E-02	1.70E-01	0.65	0.09
5	2.80E-03	2.29E-03	2.98E-03	9.41E-02	1.23	0.03

Figure Captions for Supplementary Material

Figure S1: Decay of correlation for the $\Delta\nu_{OH}$= 4 transition of the second stable conformer for (a) ethylene glycol, (b) 1-3 propanediol, and (c) 1-4 butanediol. The curves are generated using the semiclassical energy binning scheme, and the results for the hydrogen bonded (red) and free (blue) OH are presented. The best fit to an exponential decay curve is also shown as well as the resulting decay time in fs.

Figure S2: Decay of correlation for the $\Delta\nu_{OH}$= 3 transition of the most stable conformer for (a) ethylene glycol, (b) 1-3 propanediol, and (c) 1-4 butanediol. The curves are generated using the semiclassical energy binning scheme, and the results for the hydrogen bonded (red) and free (blue) OH are presented. The best fit to an exponential decay curve is also shown as well as the resulting decay time in fs.

Figure S3: Decay of correlation for the Δv_{OH}= 4 transition of ethanol. The curves are generated using the semiclassical energy binning scheme, and the best fit to an exponential decay curve is also shown as well as the resulting decay time in fs.

Figure S4: Time dependence of energy in the OH bonds calculated by the local mode model for the Δv_{OH}= 4 excitation for the OH_b in BD. NM1 is mainly OH_f stretching vibration and NM2 is mainly OH_b stretching vibration.

Figure S5: Time dependence of the energy in the 40 normal mode coordinates for the Δv_{OH}= 4 excitation for the OH_b in BD. Modes are numbered in decending order of frequency. Modes 3-10 mainly correspond to CH stretching vibrations, 11-28 mainly corresponds to CH and OH bend vibrations, 29-33 mainly corresponds to CH wag vibrations. 34-42 mainly corresponds to frame bending modes and OH torsion vibrations.

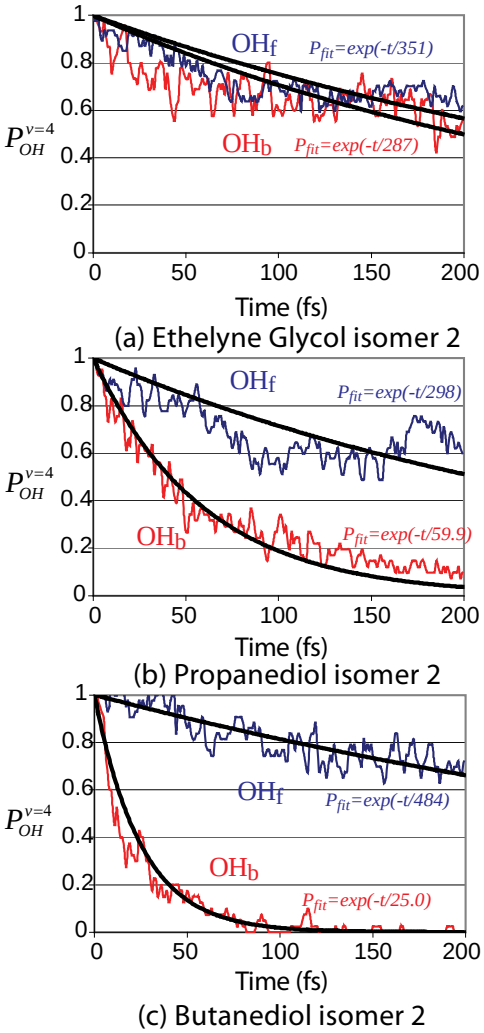

1
0.8
0.6
0.4
0.2
0
$P_{OH}^{v=4}$
OHf
P_{fit}=exp(-t/351)
OHb
P_{fit}=exp(-t/287)
0
50
100
150
200
Time (fs)
(a) Ethelyne Glycol isomer 2
OHf
P_{fit}=exp(-t/298)
OHb
P_{fit}=exp(-t/59.9)
Time (fs)
(b) Propanediol isomer 2
OHf
P_{fit}=exp(-t/484)
OHb
P_{fit}=exp(-t/25.0)
Time (fs)
(c) Butanediol isomer 2

Figure S1

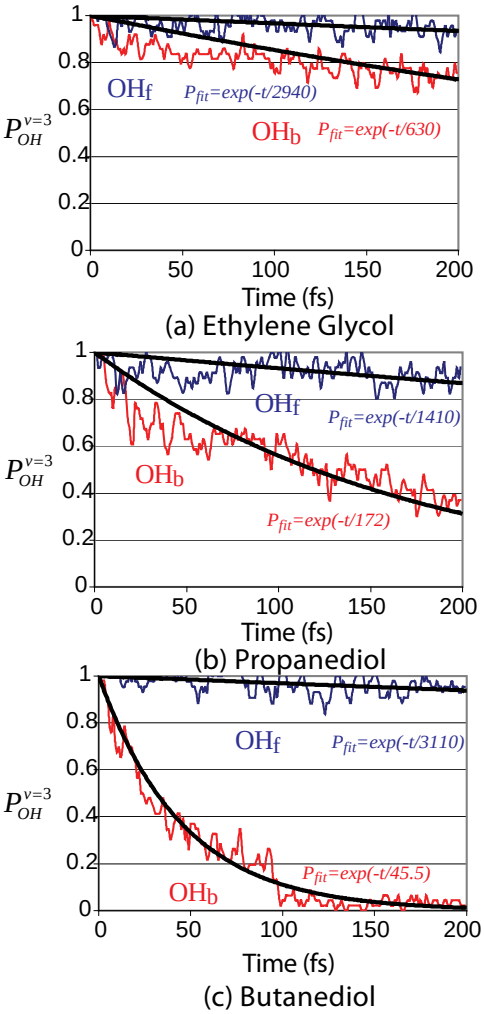


Figure S2

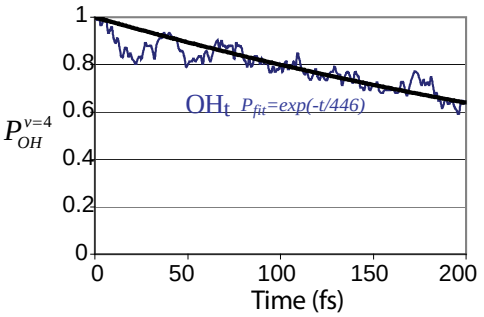
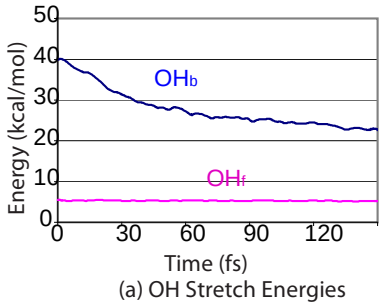


Figure S3



(a) OH Stretch Energies

Figure S4

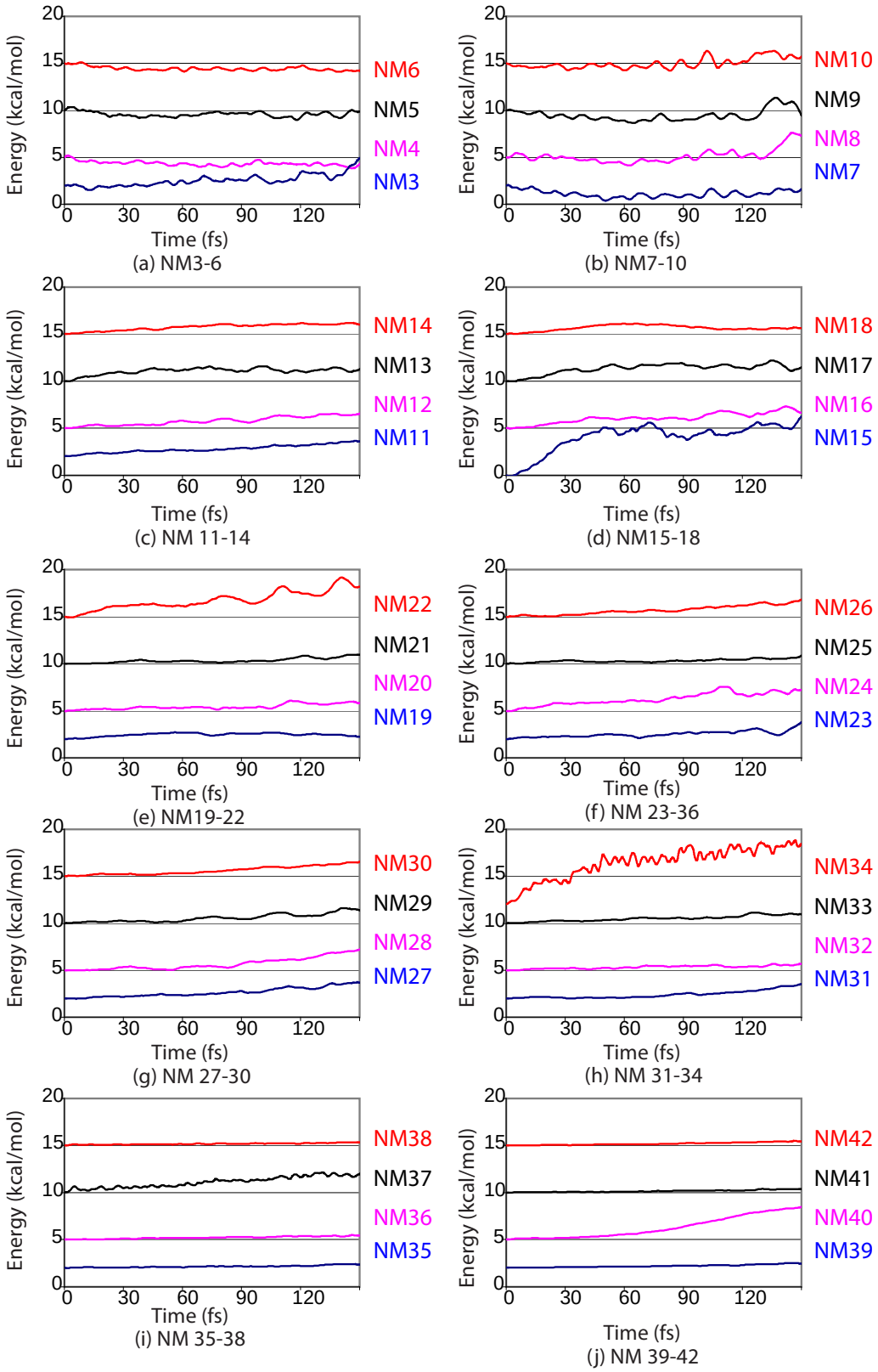

Energy (kcal/mol)
Time (fs)
(a) NM3-6
NM6
NM5
NM4
NM3
(b) NM7-10
NM10
NM9
NM8
NM7
(c) NM 11-14
NM14
NM13
NM12
NM11
(d) NM15-18
NM18
NM17
NM16
NM15
(e) NM19-22
NM22
NM21
NM20
NM19
(f) NM 23-36
NM26
NM25
NM24
NM23
(g) NM 27-30
NM30
NM29
NM28
NM27
(h) NM 31-34
NM34
NM33
NM32
NM31
(i) NM 35-38
NM38
NM37
NM36
NM35
(j) NM 39-42
NM42
NM41
NM40
NM39

Figure S5

Optimized geometries for all the molecules calculated in the paper are given in the following in Angstrom xyz format.

Optimized Cartesian Geometries calculated by B3LYP/6-31+G(d,p)

EG1

C	-0.001575	-0.003655	-0.006367
C	-0.000608	0.002417	1.512688
O	1.372098	-0.002787	-0.417609
O	0.621843	1.167746	2.037520
H	-0.520986	-0.899453	-0.377522
H	-0.517534	0.891496	-0.379128
H	-1.029941	0.000168	1.884141
H	0.499966	-0.907224	1.877627
H	1.431018	0.195952	-1.359689
H	1.496348	1.229529	1.626779

EG2

C	0.042138	-0.020687	0.040847
C	-0.022439	0.003240	1.562512
O	1.400510	0.035038	-0.415704
O	0.608750	1.158762	2.095050
H	-0.475247	-0.906536	-0.354027
H	-0.437640	0.873274	-0.367577
H	-1.065793	0.028048	1.895096
H	0.437759	-0.913970	1.969265
H	1.810547	-0.832131	-0.297776
H	1.449815	1.265319	1.625898

PD1

C	-0.009887	-0.000570	-0.010616
C	0.000269	0.008054	1.513667
C	1.407461	-0.001862	2.122859
O	0.663530	-1.188978	-0.465639
O	2.072495	-1.252408	1.988896

H	-1.042424	0.012817	-0.385965
H	0.508284	0.891351	-0.393525
H	-0.527824	0.912561	1.844959
H	-0.561297	-0.855394	1.890715
H	2.007987	0.808670	1.674785
H	1.347558	0.194017	3.198248
H	0.729402	-1.177965	-1.428553
H	1.955089	-1.543289	1.071031
PD2			
C	0.007130	-0.055326	0.026444
C	-0.001859	0.010348	1.554709
C	1.398920	0.016525	2.176873
O	0.668487	-1.228132	-0.483770
O	2.097820	-1.212120	2.004992
H	-1.014325	0.005594	-0.372837
H	0.574124	0.785990	-0.385850
H	-0.527873	0.929174	1.851331
H	-0.575608	-0.832454	1.964474
H	1.981316	0.855267	1.759488
H	1.328021	0.174563	3.257548
H	0.105524	-1.998019	-0.326304
H	2.059693	-1.432333	1.060650
BD1			
C	-0.000082	0.000051	-0.000001
C	0.000003	-0.000069	1.525525
C	1.369766	0.000009	2.233637
C	2.176417	-1.304874	2.193828
O	0.384900	-1.301170	-0.486405
O	2.763491	-1.595336	0.933460
H	-1.009485	0.232177	-0.364392
H	0.692170	0.763207	-0.383071

H	-0.541549	0.904376	1.832785
H	-0.602617	-0.851819	1.869707
H	1.995740	0.809506	1.833512
H	1.191151	0.237802	3.291667
H	3.011208	-1.225697	2.898096
H	1.541899	-2.141397	2.532174
H	0.367293	-1.300762	-1.452074
H	2.038724	-1.687431	0.289418

BD2

C	-0.009108	-0.049110	0.028651
C	-0.004032	0.022782	1.557392
C	1.370175	0.007682	2.254433
C	2.173206	-1.299193	2.188709
O	0.396724	-1.325506	-0.501202
O	2.781248	-1.556944	0.932161
H	-1.007210	0.199389	-0.355563
H	0.699423	0.669201	-0.394563
H	-0.517454	0.955566	1.829589
H	-0.631911	-0.790146	1.954292
H	1.996273	0.817268	1.855399
H	1.203357	0.236171	3.316359
H	2.996916	-1.243085	2.907842
H	1.531994	-2.143390	2.497562
H	-0.284369	-1.981995	-0.303493
H	2.073452	-1.641981	0.268105

Optimized Cartesian Geometries Calculated by MPW1PW91/6-311+G(2d,p)

EG1

C	0.007637	-0.003420	0.007760
C	0.001544	0.001711	1.515790
O	1.369522	-0.002108	-0.396726
O	0.633804	1.148048	2.036125

H	-0.512272	-0.894381	-0.364564
H	-0.507015	0.889544	-0.362928
H	-1.027186	0.008284	1.879616
H	0.485694	-0.912857	1.881662
H	1.425414	0.231770	-1.324167
H	1.488193	1.212154	1.598474
PD1			
C	0.009080	-0.009542	0.008213
C	0.005968	-0.005751	1.521297
C	1.398561	-0.000427	2.134122
O	0.667060	-1.190459	-0.445982
O	2.079275	-1.226259	1.987459
H	-1.017513	0.018652	-0.373702
H	0.535126	0.878838	-0.362780
H	-0.533572	0.887544	1.851616
H	-0.546720	-0.874429	1.889999
H	1.984557	0.825233	1.702447
H	1.328083	0.184386	3.207897
H	0.766558	-1.150823	-1.398782
H	1.948265	-1.512694	1.076388
BD1			
C	0.011261	-0.010651	0.008232
C	0.008245	-0.008723	1.522731
C	1.366951	-0.003573	2.225629
C	2.168235	-1.297678	2.184646
O	0.377021	-1.303006	-0.475992
O	2.743176	-1.586813	0.933024
H	-0.991815	0.236184	-0.354784
H	0.708733	0.745516	-0.370467
H	-0.536435	0.890204	1.827568
H	-0.590721	-0.859002	1.866118

H	1.989428	0.803736	1.825004
H	1.191516	0.235502	3.280072
H	3.001158	-1.217417	2.886397
H	1.538109	-2.131000	2.528715
H	0.377025	-1.287641	-1.435477
H	2.016573	-1.667913	0.297993

Optimized Cartesian Geometries Calculated by M062X/6-311+G(2df,2p)

EG1

C	0.000984	-0.001657	-0.000358
C	-0.001080	0.001106	1.510695
O	1.364021	0.006852	-0.397000
O	0.626954	1.154919	2.018820
H	-0.513004	-0.891960	-0.375607
H	-0.513990	0.891274	-0.365752
H	-1.025753	0.000539	1.881296
H	0.496143	-0.906477	1.870149
H	1.431526	0.194338	-1.333769
H	1.484721	1.222928	1.589410

PD1

C	-0.005578	0.002727	-0.002408
C	-0.001089	0.002643	1.513379
C	1.404520	-0.004463	2.104498
O	0.686808	-1.157162	-0.454123
O	2.040167	-1.258764	2.003133
H	-1.031584	0.001811	-0.380576
H	0.495832	0.904147	-0.371182
H	-0.533216	0.894505	1.851912
H	-0.544401	-0.869393	1.883143
H	2.005723	0.778358	1.622473
H	1.359163	0.228701	3.168157
H	0.740999	-1.152531	-1.410921

H 1.935715 -1.564024 1.096536

BD1

C 0.013281 -0.011626 0.001888

C -0.004597 0.017260 1.519679

C 1.356385 -0.000256 2.219305

C 2.183026 -1.270702 2.056568

O 0.293610 -1.339149 -0.442231

O 2.783313 -1.394500 0.786770

H -0.963921 0.295041 -0.378869

H 0.768517 0.681613 -0.382606

H -0.528851 0.928540 1.815915

H -0.615335 -0.821980 1.863858

H 1.960211 0.843465 1.873992

H 1.182542 0.151664 3.287727

H 3.001283 -1.255599 2.776974

H 1.563726 -2.147815 2.281886

H 0.190795 -1.385296 -1.394654

H 2.079052 -1.575390 0.153926

Optimized Cartesian Geometries Calculated by MP2/6-311++G(3df,3pd)

EG1

C -0.289499 -0.633382 -0.693897

C 0.297321 -0.602555 0.695740

O 0.170672 0.550009 -1.342582

O -0.159115 0.522408 1.421446

H 0.048727 -1.527241 -1.223998

H -1.379217 -0.639586 -0.629546

H -0.014328 -1.485986 1.249045

H 1.388547 -0.603779 0.621797

H -0.328747 0.675849 -2.151303

H 0.008370 1.285778 0.860219

PD1

C	-0.186628	-0.484690	-1.310038
C	0.355159	-1.068960	-0.023101
C	-0.306943	-0.486032	1.217593
O	0.059219	0.924355	-1.297876
O	0.110674	0.836852	1.497383
H	0.300748	-0.943562	-2.172867
H	-1.261493	-0.675807	-1.376287
H	0.184741	-2.147373	-0.048125
H	1.431264	-0.900752	0.033869
H	-1.396796	-0.534578	1.102414
H	-0.042444	-1.077675	2.092156
H	-0.330741	1.313553	-2.083526
H	0.067296	1.315558	0.662402
BD1			
C	0.136660	-0.365761	-1.590009
C	1.226625	0.216099	-0.711329
C	1.218454	-0.203601	0.759192
C	0.073929	0.335445	1.607316
O	-1.096283	0.315255	-1.324133
O	-1.167017	-0.294273	1.356204
H	0.401756	-0.225668	-2.639443
H	0.024919	-1.435888	-1.396554
H	2.178346	-0.093402	-1.148483
H	1.183355	1.305057	-0.792216
H	1.217013	-1.293818	0.833080
H	2.152217	0.144982	1.208064
H	0.294621	0.152244	2.657854
H	-0.004115	1.420281	1.469817
H	-1.766102	-0.024510	-1.922811
H	-1.401787	-0.070012	0.445030