

# Initial Decomposition Reactions of Bicyclo HMX [BCHMX or cis-1,3,4,6-Tetranitrooctahydroimidazo-[4,5-d]imidazo le] from Quantum Molecular Dynamics Simulations

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**Page 8: Table S1.** The bond type and bond distance cut-off table in the fragment analysis.

**Page 9:** Atomic coordinates of all TS shown in this study.

## Coordinates for structures of BCHMX

```

_pd_phase_name          'BCHMX\-\experiment'
_cell_length_a          8.54300
_cell_length_b          6.94800
_cell_length_c          8.77800
_cell_angle_alpha       90
_cell_angle_beta        102.45200
_cell_angle_gamma       90
_symmetry_space_group_name_H-M  'P 21'
_symmetry_Int_Tables_number 4

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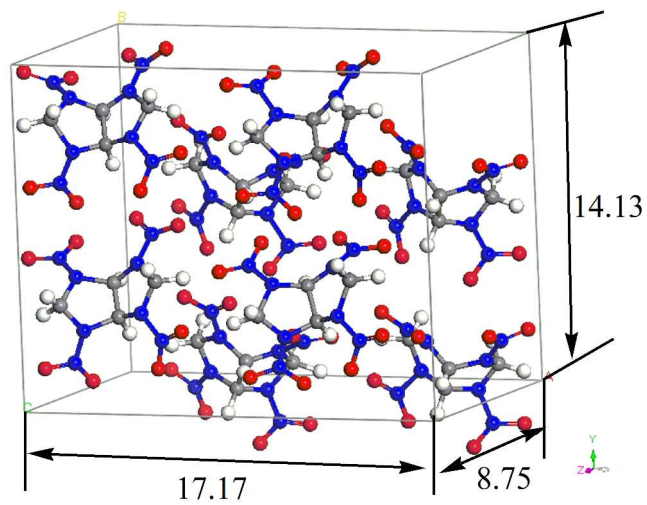
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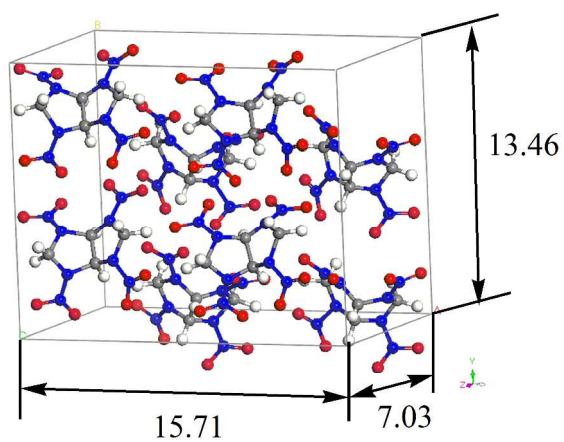
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_atom_site_adp_type
_atom_site_U_iso_or_equiv
_atom_site_type_symbol
N3      1.0    0.780500  -0.068300  0.169400  Uiso  0.020850 N
N7      1.0    0.856900  -0.248500  0.201000  Uiso  0.026780 N
N2      1.0    0.876900   0.211600  0.290100  Uiso  0.022806 N
N5      1.0    0.600000   0.410500  0.466500  Uiso  0.030360 N
N6      1.0    1.010200   0.300600  0.371100  Uiso  0.031524 N
O1      1.0    0.476300   0.505100  0.444600  Uiso  0.039737 O
O6      1.0    0.787900  -0.368800  0.261300  Uiso  0.039298 O
C2      1.0    0.749300   0.159900  0.366800  Uiso  0.018568 C
H2      1.0    0.789600   0.128400  0.477100  Uiso  0.022000 H
O3      1.0    1.001800   0.369100  0.498000  Uiso  0.041365 O
N1      1.0    0.622700   0.302200  0.345200  Uiso  0.020948 N
O4      1.0    1.122100   0.314400  0.307700  Uiso  0.050082 O
N8      1.0    0.403000  -0.062300  0.122000  Uiso  0.032270 N
N4      1.0    0.524500   0.061900  0.181700  Uiso  0.023795 N
C4      1.0    0.674000  -0.015700  0.272000  Uiso  0.017970 C
H4      1.0    0.656300  -0.122600  0.339100  Uiso  0.022000 H
C1      1.0    0.480100   0.250800  0.229100  Uiso  0.026614 C
H1A    1.0    0.385600   0.245100  0.273500  Uiso  0.032000 H
H1B    1.0    0.461500   0.340600  0.142400  Uiso  0.032000 H
O2      1.0    0.703200   0.410800  0.585500  Uiso  0.047332 O
O7      1.0    0.439700  -0.232400  0.117800  Uiso  0.042840 O
O8      1.0    0.272800   0.009400  0.072300  Uiso  0.044106 O
O5      1.0    0.980100  -0.270600  0.156100  Uiso  0.039758 O
C3      1.0    0.885100   0.093400  0.154000  Uiso  0.027026 C
H3A    1.0    0.993800   0.050600  0.157100  Uiso  0.032000 H
H3B    1.0    0.845700   0.163400  0.057800  Uiso  0.032000 H

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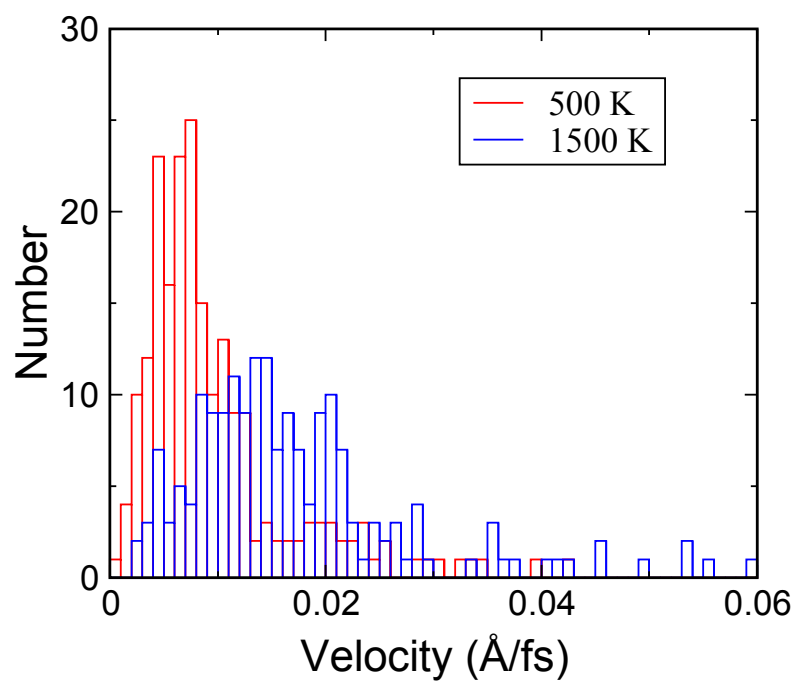


**(a) non-compressed BCHMX supercell**

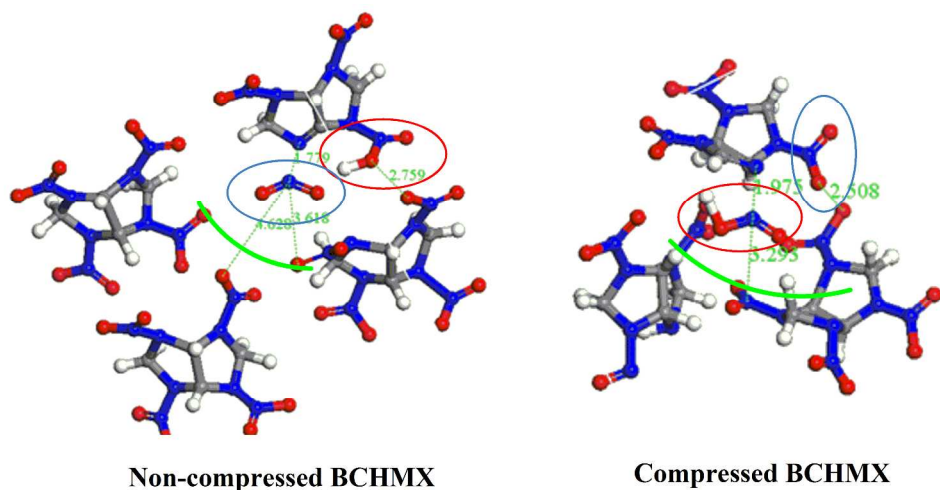


**(b) compressed BCHMX supercell**

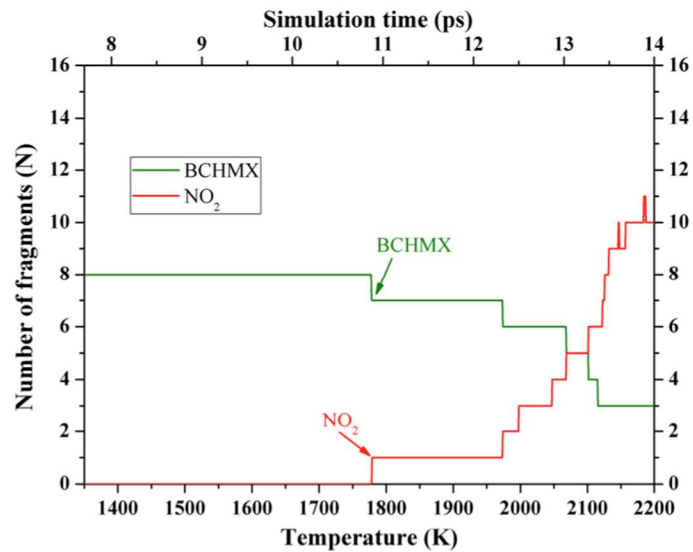
**Figure S1.** Supercell of the BCHMX crystal: (a) non-compressed BCHMX supercell; (b) 30% compressed BCHMX supercell, Unit is Å.



**Figure S2.** Velocity distribution for  $T = 500$  K and 1500 K during the cook-off simulation



**Figure S3.** Rationalization for the noncompressed BCHMX case to explain why transfer of the H to the O of an NO<sub>2</sub> group leads to release of a nearby NO<sub>2</sub> molecule rather than the expected HONO release; whereas for the compressed case the HONO is released rather than the nearby NO<sub>2</sub>. The HONO entity is indicated by the red ellipse, while the NO<sub>2</sub> is indicated with a blue ellipse. The free space available for NO<sub>2</sub> releasing reaction in the non-compressed simulation is indicated by the green arc, while the free space available for HONO release in the compressed simulation is indicated by the green arc.



**Figure S4.** Species analysis for decomposition of non-compressed BCHMX heated from 300 to 2200 K. The first decomposition reaction for BCHMX occurs at  $\sim 1770$  K (11 ps), releasing one  $\text{NO}_2$  molecule. The 2<sup>nd</sup> reaction occurs at 1970 K (12.3 ps) releasing one  $\text{NO}_2$  from the other BCHMX molecular. The 3<sup>rd</sup> reaction occurs at 2000 K releasing one more  $\text{NO}_2$  from the decomposed BCHMX fragment.

**Table S1.** The bond type and bond distance cut-off table in the fragment analysis.

<b>Bond type</b>	<b><math>r_{\text{cut-off}}</math> (Å)</b>
C-C	2.31
C-H	1.63
C-O	2.15
C-N	2.20
H-H	1.11
H-O	1.50
H-N	1.61
O-O	2.22
O-N	2.10
N-N	2.17



## Atomic coordinates of all TS shown in this study

### TS1

&zmat

H15	14.5234411948	11.8644936488	-0.5405981710
N17	15.3564106789	13.5128540048	-1.7457779207
N19	15.8200502475	12.2625793414	-1.8870500021
N21	15.7160764387	15.7121336103	-1.3991258988
N23	13.0417561838	16.5030566911	0.9150149634
N25	16.6441152205	16.7323856742	-1.1178829197
N27	13.5151474213	15.9972514753	-0.3532064323
N29	12.2415371317	12.8794660338	-0.3286572434
N31	13.0627766943	13.8243306490	-1.0581949716
O17	11.8347176130	16.7469703598	0.9730072560
O19	15.1668449531	11.3307652153	-1.1659250186
O21	16.3684239292	17.4725865651	-0.1722613612
O23	17.6155059234	16.8011928446	-1.8861381265
O25	13.8889813675	16.7077159511	1.7837375376
O27	12.8250333993	11.8469736136	0.0483091979
O29	11.0388167868	13.1122809944	-0.2460121238
O31	16.7000367253	11.9493152719	-2.6784204423
C9	14.7939631561	15.2759449857	-0.3196457730
C11	14.4478942067	13.8396481749	-0.7003643979
C13	12.5455385897	15.2029291718	-1.1269674030
C15	16.2207325218	14.6087538502	-2.2267052493
H13	15.2589683586	15.4505281926	0.6636566512
H17	11.5327500900	15.2986828905	-0.7157473540
H19	12.5635600091	15.5348609170	-2.1765590428
H21	17.2894605250	14.3998700693	-2.0491106048
H23	16.0580243546	14.7870916479	-3.3016481882

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### TS2

&zmat

N21	15.9025171817	1.3166720066	-1.3965192865
N23	13.3157525361	2.0428691563	1.0188097203
N27	13.6808284616	1.5048600602	-0.2577089929
O17	12.1137668711	2.2880657304	1.1631433596

O25	14.2243948295	2.2579062660	1.8225642703
C9	14.9675663873	0.8244385077	-0.3390706198
C13	12.6443025552	0.6873913471	-0.9515516090
C15	16.5146122682	0.2016310242	-2.1468163293
H13	15.4585974894	0.8718026578	0.6485727768
H17	11.7233007907	0.6322845823	-0.3515508104
H19	12.4144574337	1.1447305626	-1.9278228568
H23	16.5158098294	0.3864584237	-3.2320526172
N17	15.5798472669	-0.8962112231	-1.8148474364
N19	15.9724929881	-2.1440975344	-2.0726954872
N29	12.4807885606	-1.8032696836	-0.1178648963
N31	13.2546873713	-0.6169327488	-1.2028045903
O19	15.2105617303	-3.1420013269	-1.5658257243
O27	13.2188298169	-2.7882917205	0.0716155149
O29	11.2967306810	-1.7138185050	0.1354329664
O31	16.9015937303	-2.4048657182	-2.8331945006
C11	14.5774205458	-0.5152154002	-0.9095474900
H15	14.5289813753	-2.7650365599	-0.8723730033
N25	16.7994171247	2.3554361050	-1.0697158278
O21	16.4428074746	3.1172384360	-0.1712741539
O23	17.8264603978	2.4155402440	-1.7630809270
H21	17.5416780389	-0.0276553276	-1.8127149486

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**TS3**

&zmat

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N23	13.1902020481	2.0740605891	0.8668002096
N27	13.5794387220	1.4491752259	-0.3675839632
O17	11.9839471440	2.3110471469	0.9895287072
O25	14.0952697833	2.3682539978	1.6472864061
C9	14.8840907185	0.7546507921	-0.3775296752
C13	12.5425604237	0.6011967923	-1.0052338826
C15	16.2044145581	0.2618067371	-2.3838595915
H13	15.3072146725	0.8122445521	0.6407286890
H17	11.6078686362	0.6238814941	-0.4292767527
H19	12.3614657608	0.9450982033	-2.0347986612
H23	15.9000036202	0.6223894135	-3.3794919724

N17	15.3575555314	-0.8859615960	-2.0196944819
N19	16.1502570692	-2.1879426931	-1.9896266522
N29	12.5407859942	-1.7481592615	-0.2152662933
N31	13.1404622211	-0.7439966193	-1.0632398683
O19	15.5080383180	-3.1716246976	-1.3065613419
O27	13.2741497244	-2.7278096997	0.0455322407
O29	11.3558756136	-1.6339519065	0.0749411023
O31	16.9277808096	-2.4883995487	-2.8687578248
C11	14.5456244533	-0.5991197197	-0.9583010073
H15	14.7951150456	-2.7232770023	-0.7118044588
N25	16.9779479528	2.0105386547	-0.8457780138
O21	16.8208902477	2.5561477426	0.2469626516
O23	17.9625819384	2.0806445219	-1.5948548218
H21	17.2792494575	0.0265707463	-2.3964108904

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**TS4**

&zmat

H15	14.6808087927	12.8209330142	-0.3595676832
N17	14.6980662101	13.8831680137	-2.1482726400
N19	16.0433683613	12.4140709948	-1.5654085248
N21	15.4761024484	15.8140511934	-1.0127363832
N23	12.6600499298	16.8618280804	0.6636250285
N25	16.7076939503	16.0136777818	-0.3100498906
N27	13.0831022329	16.0161460318	-0.3988480389
N29	12.1239647384	12.9831576069	0.1441229680
N31	12.6049785108	13.7867828116	-0.9730188042
O17	11.4639414932	17.1735216508	0.6611865555
O19	15.5598357024	12.0134795171	-0.4427435819
O21	16.6339534354	16.1982763615	0.9052959142
O23	17.7240047643	16.0373469882	-1.0131530416
O25	13.5396375957	17.2412014316	1.4393413075
O27	12.9355840346	12.1727420627	0.6052464478
O29	10.9483761357	13.1285943094	0.4620725674
O31	16.9538616338	11.8708040862	-2.1335312099
C9	14.3526958214	15.2953300763	-0.2330369713
C11	14.0387928172	13.9743135218	-0.9650072602
C13	12.0456525520	15.1468552794	-1.0211309491

C15	15.5582425159	15.0532659504	-2.2826962802
H13	14.6390021015	15.2514206385	0.8298446883
H17	11.0944012502	15.2171204734	-0.4764212476
H19	11.9008931465	15.4265334535	-2.0749786351
H21	16.6035412158	14.8284012006	-2.5390158403
H23	15.1233929545	15.6584870492	-3.1000949129
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**TS6**

&zmat

N2	2.7275553820	2.8069286700	4.9449908672
N4	2.1366252110	1.4765335503	4.7834561761
N6	1.2742196861	4.5999042719	5.3045067898
N8	2.3053542969	7.2762191685	3.6994263246
N10	-0.1588789550	4.2977808614	5.3213038736
N12	2.7531518500	5.9657236886	3.9487724577
N14	5.2607970841	3.5400538194	3.2500052101
N16	4.0882400003	4.2542850215	3.5375459782
O2	3.2028620225	8.1194409057	3.5516489675
O4	2.1433540673	1.0083877580	3.6471887450
O6	-0.8128348192	4.7164062691	4.3683311868
O8	-0.5590483833	3.7164750503	6.3233381500
O10	1.0819370839	7.4293550574	3.6801409109
O12	5.1123466705	2.3379465594	3.0175897391
O14	6.2994856241	4.2176663556	3.2430867574
O16	1.7590715011	0.9471321893	5.8229228581
C2	1.8350533604	4.8281612879	3.9798258670
C4	2.7937672561	3.5996441486	3.7233472009
C6	4.1038057404	5.6192735321	3.8631197480
C8	2.1325593444	3.6359847142	6.0078517657
H2	1.0203262728	4.9635076248	3.2531691122
H4	2.5424312071	2.9668546662	2.8598788817
H6	4.7858919957	6.2908177397	3.3343352751
H10	1.5644203251	3.0329558510	6.7271056152
H12	2.9289462514	4.1792322868	6.5374868695
N33	5.2881372141	5.5111124372	6.3390857028
N35	5.7292676426	4.0537540479	8.0732822576
N37	6.9166327971	7.1337288321	6.7608885766

N39	5.0124698492	9.6034170217	8.6309843927
N41	8.2402106282	7.4157025261	7.1476813607
N43	5.3360404687	8.8270256360	7.4474623329
N45	2.3833697017	7.3173808664	7.2580075670
N47	3.6970841614	7.3699724888	6.6507336783
O33	4.2259413837	10.5329394927	8.4545898859
O35	4.7307379059	3.8283706978	8.7456328481
O37	8.3839640630	8.2370649100	8.0588174563
O39	9.1164019173	6.8336471040	6.4962967755
O41	5.6087403656	9.3053861244	9.6649940921
O43	2.0883976820	6.2549725297	7.8147828450
O45	1.6633857643	8.2959582517	7.0788144537
O47	6.7326889630	3.3821001266	7.9004151150
C17	5.8537606337	7.4782890282	7.6942355329
C19	4.7055648044	6.5079787713	7.2740195792
C21	4.2724138566	8.7179185965	6.4503972078
C23	6.6886859315	5.8578891993	6.0597295133
H8	4.7253420405	5.5411826664	5.3752737344
H25	6.1750435366	7.4078281191	8.7450204220
H27	4.2394978635	5.9767395331	8.1189334542
H29	3.5148795046	9.5029751806	6.5635666281
H31	4.7121249762	8.7612236049	5.4428673547
H33	7.3652293008	5.0728547299	6.4472735863
H35	6.8634079436	5.9577885412	4.9785372717

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**TS7**

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N50	9.8211349906	9.8543064822	3.8054424747
N52	8.2735060017	8.4738132054	3.2997300884
N54	8.7176383649	11.8709190726	3.5108793949
N58	7.4062813672	12.4152589812	3.4936273453
N60	10.4887910289	12.7340775084	2.1212045779
N62	12.5792412718	9.8473505365	2.6900625576
N64	11.5568447938	10.7560947940	2.3884891287
O52	8.2542482004	7.4380270644	2.6798125832
O54	7.1051377013	13.0963993373	2.5115083882
O56	6.7293165079	12.1828950300	4.5018472425

O60	12.3136087458	8.6538818785	2.5327518298
O62	13.6556593550	10.3534823209	3.0349384856
O64	7.3206469186	8.8871736799	4.0410333401
C26	9.4298871486	11.7149036790	2.2472065179
C28	10.1601233198	10.3373622572	2.4495848159
C30	11.7143501160	12.1864252897	2.6973880904
C32	8.9964882320	10.7533601973	4.3927853759
H38	8.7533006174	11.7943661771	1.3851690465
H40	9.9535074880	9.5665331810	1.6948626486
H42	12.6054001713	12.6108078013	2.2208531478
H44	11.7336304936	12.3847059708	3.7843875620
H46	7.9172287168	9.9571887666	4.4359737493
N56	10.6397965777	13.2907164639	0.7828478910
O50	11.7316690696	13.7994796534	0.5368050179
O58	9.6398621930	13.2693124957	0.0665630332
H48	9.1277263382	10.9779397921	5.4620712561

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**TS8**

&zmat

N5	7.1115210430	1.9504605105	2.1485214255
N7	4.1143208230	3.0964052197	3.2759788162
N11	4.7437742345	2.2540782152	2.3114404020
N15	4.1954533861	0.1003614061	1.6318330630
O1	2.9958724434	3.5171323945	2.9709468711
O9	4.7758970038	3.3631125646	4.2814238747
O13	2.0441751184	-0.2676730295	2.2581473485
C1	5.8716614859	1.4397113342	2.7633042810
C5	3.8847822801	1.5089796036	1.3742245480
C7	7.4668625792	1.1054718236	1.1522510211
H1	5.9376027719	1.4702611272	3.8605631209
H5	2.8225594029	1.7310983551	1.5392826954
H7	4.1665024925	1.7514939996	0.3376824534
H9	8.5827602416	0.6571974925	1.7315891947
H11	7.8681126169	1.5196053953	0.2158461622
N1	6.5355758895	-0.0061065941	1.0397010532
N3	7.0365205082	-1.2669696743	0.6307662451
N13	3.2105535121	-0.6327572911	2.4020130605

O3	6.3449008110	-2.2476750470	0.9133963398
O11	3.6251140893	-1.5887480204	3.0576263691
O15	8.0933330621	-1.2314608458	-0.0101780129
C3	5.5684318412	0.0328818637	2.1370377501
H3	5.6634430320	-0.8313962954	2.8100200996
N9	8.5080646161	1.1396209556	3.5712255156
O5	8.7154191678	1.3360084786	4.7453284529
O7	9.2947628711	0.4933313697	2.8012693989
&			