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Electronic Supplementary Information

Interactions between Hydrogen and Tungsten Carbide: A First Principles Study

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1. Supporting Figures

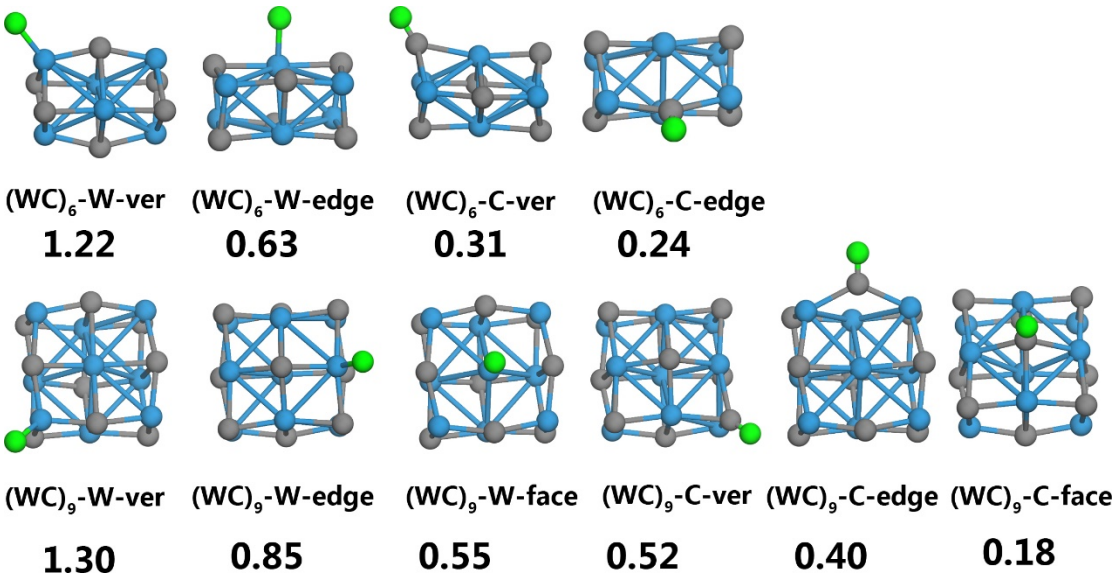

Figure S1

Atomic H adsorption energies (in eV) on various W and C sites for $(WC)_6$ (vertical and edge sites) and $(WC)_9$ (vertical ,edge and face sites). The adsorption energy is defined as $E_{ads} = E_{(WC)_n} + 1/2E_{H_2} - E_{(WC)_n H}$

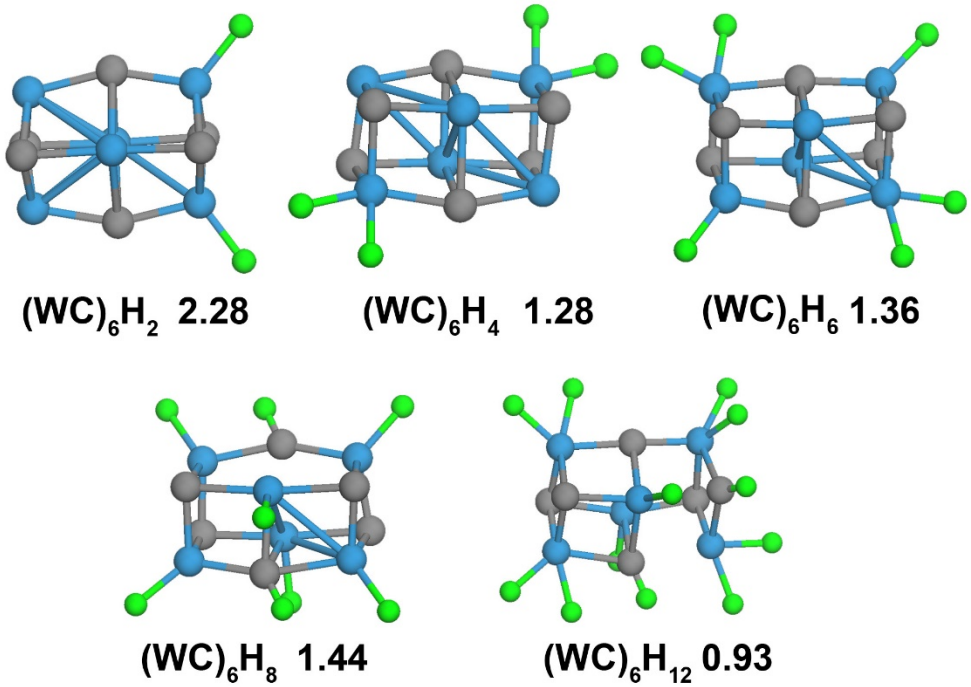

Figure S2

Local minimum structures of H_2 chemisorbed on $(WC)_6$; adsorption energies (in eV) are provided.

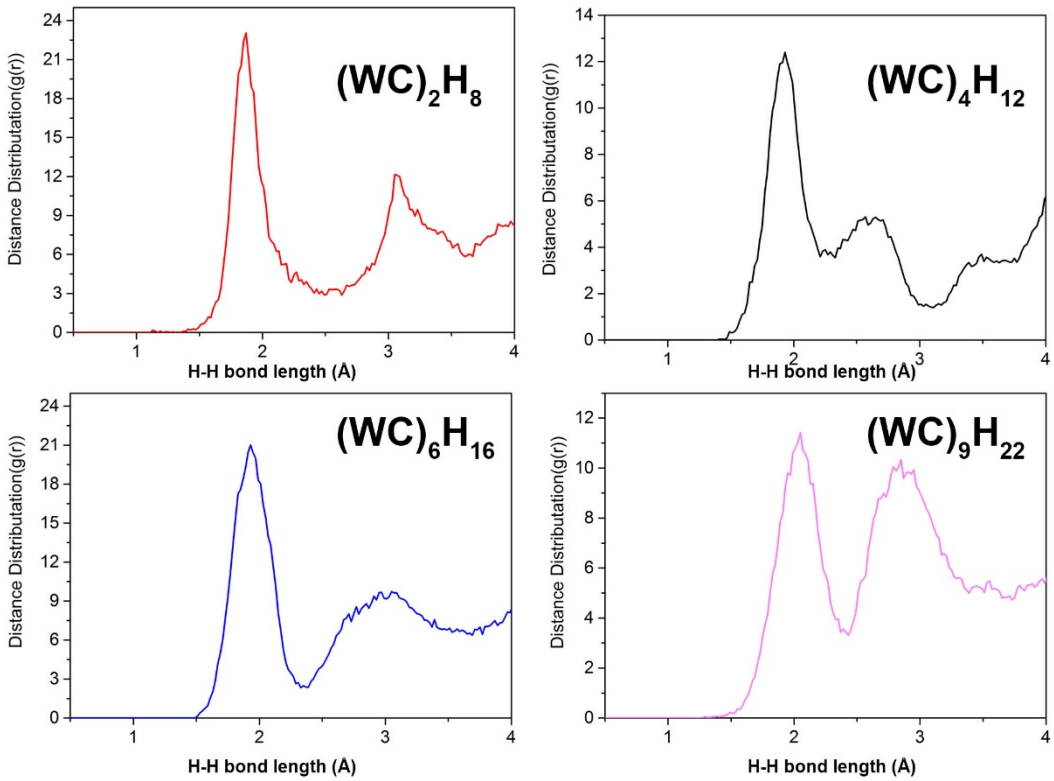

Figure S3

The calculated H-H bond length distributions of the fully saturated $(WC)_n$ (n=2, 4, 6, 9)hydrides. No H-H bond peak (ca. 0.74 Å) was detected. g(r) was obtained by tabulating all the H-H distances at each step of the MD trajectories fitted with Gaussian functions.

2. Cartesian coordinates of selected atomic clusters (in Å)

2.1 Most stable configurations of $(WC)_n$ (n=1-10)

WC

C	0.00000000	0.00000000	0.00000000
W	0.00000000	0.00000000	2.07000000

$(WC)_2$

C	0.00000000	0.00000000	0.00000000
W	0.00000000	0.00000000	1.87698252
C	1.87324210	0.00000000	1.81559918
W	1.87334073	0.00003289	-0.06188253

$(WC)_3$

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	3.00796815
C	2.60375500	0.00000000	1.49836819
W	-0.76873446	-0.88472943	1.49726527
W	1.45128612	-1.30509769	0.48753937
W	1.69649428	-0.87895878	2.91577712

$(WC)_4$

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.74493594
W	1.45355743	0.00000000	1.37244447
W	-1.44910708	-0.11291826	1.37244799
C	-1.44690316	1.88626213	1.37239130
C	1.29599625	1.99285506	1.37243365
W	-0.07757500	1.99596335	-0.07995636
W	-0.07756324	1.99605600	2.82486680

$(WC)_5$

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	3.05837870
C	2.91686404	0.00000000	2.57544567
C	1.24179505	-2.25022648	2.16965646
W	-0.38475747	-1.20330717	1.57932809
W	1.26672096	0.98413964	1.54012870
W	2.42579228	-1.01285860	0.89265364
W	1.58894460	-0.99142072	3.64850562
C	2.72867232	-0.51336104	-1.05664953
W	1.40592097	0.79726821	-1.09319437

$(WC)_6$

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.70467898
W	1.47206556	0.00000000	1.33509940
W	-1.42417465	0.36032271	1.36809525
C	-1.73161908	2.36196253	1.50299557
C	2.27600755	1.86169442	1.18817409
W	0.36936391	2.09724282	0.09686485
W	0.17440419	2.12647134	2.59488951
C	0.54364333	4.22373923	-0.01319629
W	1.96787745	3.86331128	1.32346084

C	0.54357205	4.22361902	2.69150434
W	-0.92823996	4.22386103	1.35627401

$(WC)_7$

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	3.54709725
C	2.54831926	0.00000000	1.76107852
C	0.71318266	-2.96894547	3.18794468
C	2.79892406	-3.00267313	0.93491688
C	3.67993918	-2.27735519	3.41099353
W	-0.82289326	-1.72392457	2.90718299
W	0.66564082	0.69226607	1.77102182
W	1.01643117	-1.84417849	1.00435688
W	1.81290907	-1.10461267	3.48159524
W	2.50673727	-3.71151473	2.76104263
W	3.88335512	-1.46470211	1.63956095
C	-1.28054950	-2.09916449	0.97527321
W	-0.80992941	-1.52501628	-0.76011896

$(WC)_8$

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	3.15679357
W	1.60680839	0.00000000	1.74278473
W	-1.16168969	0.30786766	1.59152337
C	-0.91923895	2.21406155	1.93807692
C	2.50317383	1.68353545	2.67142030
W	0.72307132	2.22104560	0.55438936
W	0.49459295	1.92824272	3.34094032
C	1.16305889	4.35833911	0.74343801
W	2.32273589	3.79203198	2.27057059
C	3.05525779	-0.25768023	0.25990951
W	1.72045731	0.31867028	-1.04585811
C	2.26605898	2.25675959	-1.26587886
W	3.35137259	1.77216740	0.73470012
C	3.79616363	3.86838876	0.93428519
W	2.56511998	4.09903049	-0.59489631

$(WC)_9$

C	0.00000000	0.00000000	0.00000000
W	0.00000000	0.00000000	2.22727381
C	4.60940388	0.00000000	0.76575123
C	3.99181293	-2.16306001	2.84515000
W	3.85397786	-0.04300972	2.89110888
W	4.17938593	-2.00203128	0.91813789
C	2.28085859	-2.39738347	0.36721081
C	1.78169648	-0.03012804	3.41282219
W	2.24409505	-0.03850391	0.74613352
W	1.90530662	-1.98585423	2.55700910
C	-0.16751579	-2.11516182	2.11661469
W	0.30973471	-1.98250851	0.24439331
C	4.05597228	2.07142779	2.86394624
W	4.22389477	1.97135595	0.93703986

C	2.32657698	2.38980992	0.39629608
W	1.95059351	1.94553723	2.55500774
C	-0.12251363	2.11286843	2.11039408
W	0.36275214	1.98705233	0.23770286

$(WC)_{10}$

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.93130916
W	1.32582143	0.00000000	1.39603636
W	-1.50525671	0.57299759	1.42601038
C	-1.68288639	2.51592268	0.61737694
C	2.17157459	1.77840387	1.02102577
W	0.22451602	2.07682410	-0.13519642
W	0.22702219	2.30916610	2.62328734
C	0.82770559	4.07596197	-0.35396535
C	0.90603298	4.52588979	2.55048856
W	2.08611905	3.78216933	1.08709099
W	-0.75176021	4.33889196	1.10099857
C	-2.85285587	0.77216606	3.00758125
C	-2.19152784	2.96433784	4.79660705
W	-2.43740519	2.85201736	2.73490224
W	-1.32384326	0.81574323	4.24674075
C	-2.00284290	4.94175357	2.65040383
C	0.39737607	2.45881662	4.73064315
W	-0.57523574	4.51905232	3.93766856
W	-0.83055103	2.80594843	6.11361314

2.2 All states of H_2 dissociation and H diffusion on $(WC)_6$

R_1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.69225887
W	1.46189257	0.00000000	1.33618014
W	-1.41515103	0.34884131	1.35146218
C	-1.62444587	2.39104227	1.37949506
C	2.24985264	1.87236695	1.24781252
W	0.29176891	2.13799727	0.10636791
W	0.21084462	2.15323745	2.56797437
C	0.55465215	4.25702736	-0.00114732
W	1.98187380	3.86787521	1.33501196
C	0.51785471	4.25272343	2.68467848
W	-0.93217214	4.34316829	1.34524385
H	-1.54002977	6.14029759	1.48220474
H	-2.30905650	5.62984001	1.53753605

P_1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.69302500
W	1.45224187	0.00000000	1.34470151
W	-1.42564689	0.35599391	1.34935310
C	-1.58808327	2.43993204	1.35213209
C	2.22856952	1.86510260	1.32098042
W	0.21452053	2.13838033	0.11216362

W	0.20280382	2.15847778	2.57611799
C	0.55181434	4.21432167	0.00606999
W	1.98779353	3.84777713	1.34147885
C	0.58777136	4.20189406	2.70198588
W	-0.93335758	4.45464222	1.37129333
H	-1.19916796	6.20525792	1.50768169
H	-2.64773806	4.84631431	1.36185002
P_2			
C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.71718739
W	1.42271042	0.00000000	1.36813981
W	-1.39240138	0.38445183	1.34786261
C	-1.57347479	2.45324022	1.28275129
C	2.14191162	1.91044466	1.32927774
W	0.23109228	2.14867879	0.10814080
W	0.21667079	2.16374542	2.67119929
C	0.50431781	4.29303809	-0.02969761
W	1.86982687	3.94683227	1.34197141
C	0.49215419	4.29859636	2.68744716
W	-0.96892939	4.37682016	1.30747353
H	-1.02814499	2.31498688	3.89557053
H	-2.31963803	5.55595417	1.27090330
P_3			
C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.71217547
W	1.42457209	0.00000000	1.35625122
W	-1.38673564	0.36353852	1.35494122
C	-1.56511664	2.45072971	1.36684902
C	2.10328748	1.97835811	1.34271179
W	0.27520470	2.16594920	0.12024848
W	0.24081224	2.17245958	2.59368134
C	0.49952362	4.31868184	-0.01103852
W	1.94530516	4.01636226	1.35107137
C	0.52974982	4.31903225	2.71177857
W	-0.92205583	4.39967836	1.35487307
H	3.53757411	4.84235090	1.34841322
H	-2.12146349	5.73178621	1.31754378
P_4			
C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.71918133
W	1.46509626	0.00000000	1.33028750
W	-1.35660285	0.47136651	1.34625808
C	-1.52025546	2.53855143	1.38349508
C	2.60859448	1.70270136	0.79720065
W	0.50404906	2.10871917	0.10609173
W	0.22719056	2.14997097	2.62975080
C	0.80166125	4.27881821	0.02018194
W	2.12577445	3.70469424	1.36211832
C	0.72912640	4.19450268	2.73752580

W	-0.69489402	4.38552095	1.32605188
H	3.55836828	1.50069409	0.24151177
H	-1.89872408	5.71909116	1.29649733
P_5			
C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.70741350
W	1.47220974	0.00000000	1.34465080
W	-1.39417720	0.31162618	1.36029163
C	-1.69610529	2.36649793	1.40990097
C	2.01230984	1.96123850	1.30962719
W	0.18256348	2.14957116	0.11919008
W	0.13310031	2.17842094	2.60056660
C	0.31601788	4.32840983	0.01262621
W	1.71008489	4.01618094	1.35968023
C	0.31578857	4.32760052	2.71978987
W	-1.15632411	4.32777635	1.37504077
H	2.92730310	-1.04323954	1.26013745
H	-2.61234951	5.37005199	1.45680782
TS_1			
C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.69086369
W	1.46110634	0.00000000	1.33793689
W	-1.41550070	0.34821453	1.35123639
C	-1.61597830	2.39330743	1.37747442
C	2.25118088	1.87106746	1.26335510
W	0.28625827	2.13959441	0.11077359
W	0.21482991	2.15690367	2.57016078
C	0.56617725	4.25347749	-0.00079353
W	1.99107200	3.86633279	1.33753242
C	0.53506938	4.25693667	2.68720759
W	-0.92626222	4.35173954	1.35136217
H	-1.52698141	6.11593768	1.45701108
H	-2.34092175	5.54408550	1.50600361
TS_2			
C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.77680470
W	1.43931804	0.00000000	1.40020405
W	-1.36006093	0.38013805	1.37182206
C	-1.53035876	2.38948915	1.22899607
C	2.27686886	1.87195816	1.39921364
W	0.24698749	2.11440039	0.04815487
W	0.45773216	2.16684499	2.62061068
C	0.66333009	4.18713459	-0.11548657
W	2.13961183	3.84834308	1.12922805
C	0.96154166	4.18931600	2.60735319
W	-0.81103745	4.23554862	1.39809862
H	-2.35935685	5.10252601	1.48274942
H	-1.24162780	3.79804106	3.12541251
TS_3			

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.72461721
W	1.44391169	0.00000000	1.35071503
W	-1.40161733	0.43505554	1.36326425
C	-1.55778168	2.51683591	1.35763498
C	2.20891592	1.91088480	1.26474559
W	0.33521212	2.12281015	0.09577589
W	0.22552480	2.13631857	2.61110011
C	0.60917546	4.15443683	-0.03433382
W	1.94755735	3.96788649	1.37858952
C	0.54843272	4.14984940	2.79155000
W	-0.79879783	4.46751646	1.36943130
H	0.72865412	5.86131046	1.40455040
H	-2.03978434	5.75128959	1.47941869

TS_4

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.75773075
W	1.53604613	0.00000000	1.39855879
W	-1.31902383	0.39218468	1.38736031
C	-1.43951210	2.43535610	1.50185430
C	2.24942614	1.93382469	1.24141102
W	0.36823538	2.13279913	0.16404981
W	0.53953914	2.04517971	2.68202118
C	0.64719017	4.31195175	0.08644364
W	2.12283331	3.96882271	1.32662585
C	0.87457344	4.21741460	2.79639657
W	-0.70793609	4.31318945	1.54942821
H	2.21022054	0.56136330	3.10372981
H	-2.10671815	5.42761689	1.63666460

TS_5

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.71861826
W	1.42664705	0.00000000	1.32926921
W	-1.38912052	0.43257766	1.36101219
C	-1.61140618	2.50368173	1.40555897
C	2.30384935	1.85483268	1.01041557
W	0.31135635	2.15022991	0.08222710
W	0.10792415	2.17890854	2.64425207
C	0.49747160	4.25480086	-0.03078587
W	1.93652896	3.76555609	1.34462923
C	0.45883839	4.23932366	2.74144238
W	-0.92526980	4.40848186	1.32316213
H	3.53954212	2.78662447	1.13170789
H	-2.00998759	5.84188782	1.23939447

TS_6

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.72079902
W	1.52669010	0.00000000	1.32479957
W	-1.37539033	0.40598927	1.36436635

C	-1.53897620	2.45792241	1.43071986
C	2.41240167	1.73576399	1.05775435
W	0.43406174	2.06815289	0.09710330
W	0.23690901	2.10161716	2.63587766
C	0.74615498	4.21094982	0.01555372
W	2.09900502	3.77385560	1.35000375
C	0.72640943	4.18315651	2.72790199
W	-0.74846730	4.31434468	1.35919776
H	3.31432793	0.55691128	1.16155468
H	-2.13257974	5.45207109	1.32611278

2.3 Fully H-saturated $(WC)_n$ (n=2,4,6,9) clusters

$(WC)_2H_8$

C	0.00000000	0.00000000	0.00000000
H	0.00000000	0.00000000	1.09804002
W	1.59531600	0.00000000	-1.35442326
H	2.30182064	1.55924459	-1.55808810
H	2.33502485	-1.51057957	-1.74819288
H	3.32257434	-0.03797546	-1.24261539
C	0.35913935	0.01987831	-2.81735329
H	0.35781983	0.02139286	-3.91586765
W	-1.24101102	0.12966590	-1.45692556
H	-2.96124461	0.29969826	-1.58320086
H	-1.70560980	1.70974367	-0.96730647
H	-2.01272917	-1.32511747	-0.95786785

$(WC)_4H_{12}$

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.99315354
W	1.36914463	0.00000000	1.44973442
W	-1.55940103	0.44592457	1.54899021
C	-1.42201497	2.51313699	2.23671049
C	1.50221482	2.09815916	1.51863762
W	-0.30163618	2.13190307	0.29497909
W	0.23864152	2.09158141	3.20971051
H	0.51788212	2.86520386	4.75547541
H	-0.64277279	2.04147664	-1.40772845
H	-2.53732677	-0.39241532	0.37516768
H	2.60255132	-1.23594298	1.32878445
H	-1.49418720	3.27942220	-0.24719065
H	-3.25109089	0.87128449	1.53602069
H	2.36678671	2.73741861	1.33737001
H	2.99850620	0.53008300	1.13465120
H	-2.15731276	3.29744689	2.44592404
H	0.04066908	-0.64002427	3.89183759
H	1.37862776	3.40280603	3.23991423
H	-0.00879892	-0.56655551	-0.93645805

$(WC)_6H_{16}$

C	0.00000000	0.00000000	0.00000000
H	0.00000000	0.00000000	1.09777904
C	1.69804184	0.00000000	-2.34233433

H	2.73776852	-0.11806404	-2.67365081
W	0.61472353	-1.46219444	-1.44109426
H	1.25529228	-2.20823325	0.00351136
H	1.05336273	-3.15190074	-1.61047441
W	0.77156209	1.46380220	-1.15100350
H	2.44872503	1.83699349	-0.83206068
H	1.06630429	3.11115204	-0.61741041
C	-1.07558094	1.98390679	-2.23091022
H	-0.70769500	2.89592433	-1.64961125
C	-0.98278185	-1.55790483	-2.89213735
H	-0.60222520	-2.62196474	-2.78605688
W	-1.72400935	-0.15067387	-1.39318317
H	-2.51638976	-1.45649349	-0.52962055
W	-0.16332688	0.51358445	-3.49089006
H	0.55602652	1.72275320	-4.55583827
C	-3.62959782	0.22177552	-2.43627449
W	-2.69363569	-1.03767435	-3.83455265
C	-1.98305959	0.62575697	-4.82279958
H	-2.02850019	0.82222480	-5.90548874
W	-2.72105191	1.89222790	-3.33804382
H	-3.28167312	3.48736680	-3.78296437
H	-4.32874841	2.28122295	-2.77881545
H	-2.93569649	-2.59006830	-4.60315239
H	-4.59996027	0.13043658	-1.94651928
H	-4.32736761	-1.63249863	-3.72804476

$(WC)_9H_{22}$

C	0.00000000	0.00000000	0.00000000
H	0.00000000	0.00000000	1.16002885
C	1.73497938	0.00000000	-2.40985096
H	2.77694870	-0.04650287	-2.73833964
W	0.51105838	-1.56131815	-1.41907199
H	1.97482482	-2.46964349	-1.75128955
W	0.89988309	1.33347465	-1.15352372
H	2.24968101	1.04529708	-0.08445068
H	1.59300609	2.88167505	-0.65685775
C	-0.79175391	1.84442650	-2.48166362
H	-0.31674494	2.81058590	-2.10567024
C	-0.56604031	-1.95560762	-3.27767045
H	-0.10265882	-2.69553140	-3.94421518
W	-1.80241411	0.20550392	-1.32682270
H	-2.45545461	1.43389228	-0.25991768
W	-0.09121386	0.11217241	-3.64303916
H	1.22082535	-0.44174568	-4.66293481
C	-3.62613205	0.42332725	-2.60154215
W	-2.51195605	-1.06596103	-3.83494824
C	-1.76097525	0.60582329	-5.05702587
H	-1.80710599	0.71016113	-6.15052091
W	-2.39977297	1.88889308	-3.68578875
H	-3.49091344	3.24274796	-4.00852066

H	-1.53062396	3.22713986	-4.41535784
C	-0.34255782	-3.21492703	-0.29520773
H	-0.08953287	-4.24658135	-0.03049670
W	-1.05062729	-1.70210685	0.86696852
H	-1.75668586	-3.04764832	1.74195245
H	-0.72162939	-1.45867548	2.58813187
C	-2.78766050	-1.44681667	-0.10762387
H	-3.80115949	-1.49406024	0.42688739
W	-1.93981013	-2.68631971	-1.77135144
H	-1.51981326	-4.31369152	-2.27711959
C	-3.88865271	-2.52266910	-2.84343572
H	-4.49731231	-3.34524346	-3.24385180
W	-4.40995484	-1.10720724	-1.56358782
H	-5.86287145	-0.70376247	-2.46226395
H	-5.79201046	-1.13772614	-0.45659802
H	-4.26585371	1.33556116	-2.87757534
H	-2.43138982	-2.07050826	-5.27481655