Supporting Information

Full citation of Ref. 29

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B3LYP/6-311+G optimized structures**

Cycloheptatriene (**1**, *C*s)

C	-0.00243310	-0.45875802	1.48498005
C	-1.22300212	0.24686098	0.95117546
C	1.21987860	0.24686098	0.95517806
C	-1.52771871	0.24901298	-0.36274157
C	1.52889919	0.24901298	-0.35773338
C	-0.67919216	-0.25237502	-1.42007470
C	0.68384201	-0.25237502	-1.41784141
H	-0.00186685	-1.50114102	1.13938051
H	-0.00422046	-0.46982602	2.57584658
H	-1.87928211	0.75274298	1.65311911
H	1.87385485	0.75274298	1.65926853
H	-2.47696710	0.67951798	-0.67210431
H	2.47915625	0.67951798	-0.66398382
H	-1.17413586	-0.53149702	-2.34652090
H	1.18181897	-0.53149702	-2.34266073

Cycloheptatriene (**1**, C_{2v})

C	0.00000000	0.00000000	-1.68474184
C	0.00000000	1.30724900	-0.93141684
C	0.00000000	-1.30724900	-0.93141684
C	0.00000000	-1.57659400	0.38258716
C	0.00000000	1.57659400	0.38258716
C	0.00000000	-0.67338400	1.52753116
C	0.00000000	0.67338400	1.52753116
H	0.86414100	0.00000000	-2.36812084
H	-0.86414100	0.00000000	-2.36812084
H	0.00000000	2.17166400	-1.59307784
H	0.00000000	-2.17166400	-1.59307784
H	0.00000000	2.63098400	0.64723916
H	0.00000000	-2.63098400	0.64723916
H	0.00000000	-1.16506700	2.49597616
H	0.00000000	1.16506700	2.49597616

Planar seven-membered cyclohepatriene (**2**, C_1)

C	-0.28538921	-1.11291781	0.71420981
C	1.21804687	-1.02224267	0.70587379
C	-0.59350060	0.38014679	0.72902654
C	1.47447584	-0.13385573	1.95213644
C	1.45977461	-0.12765328	-0.55625732
C	0.22930519	0.82275748	-0.56434915
C	0.23878203	0.81964075	1.98037315
H	1.77069044	-1.95946133	0.69259110
H	2.42089793	0.40603538	1.87685459
H	1.51285727	-0.75321045	2.85005955
C	1.57010903	-0.93995159	-1.83102247
H	2.40033463	0.41315608	-0.44678394
H	-0.39175289	0.60273813	-1.43435237
C	0.49809840	2.30943919	-0.61734027
H	-0.36043321	0.66272598	2.87876134
H	0.51264909	1.87682930	1.95191467
C	-2.00798051	0.86172759	0.73612565
C	-1.05399061	-2.20890137	0.72715132
C	-3.15640536	0.16028614	0.75618303
C	-2.50368464	-2.28893694	0.74911072
C	-3.39548330	-1.27395578	0.76343548
H	-0.53545565	-3.16530331	0.72403528
H	-2.90795928	-3.29684725	0.75417867
H	-4.44488362	-1.55371732	0.77921839
H	-4.06495387	0.75711985	0.76520849
H	-2.10038502	1.94438139	0.71933378
O	0.80780628	-0.92578210	-2.76432114
O	2.67993747	-1.72203040	-1.81531458
H	2.69523105	-2.21197112	-2.65135214
O	-0.35543376	3.14765228	-0.77702836
O	1.80403583	2.64866925	-0.44702678
H	1.84945029	3.61595576	-0.49808077

Norcaradiene (**3**, *C*s)

C	-0.23248929	-0.95877822	-1.43439902
C	0.61905703	0.23696178	-1.09712406
C	-0.93390676	0.23696178	-0.84541764
C	1.46431845	0.23395878	0.10510571
C	-1.35615233	0.23395878	0.56225134
C	0.95309690	0.04955578	1.34053144

C	-0.48087572	0.04955578	1.57295161
H	-0.13100851	-1.83705922	-0.80828877
H	-0.40286387	-1.15643422	-2.48556626
H	0.98333657	0.81111078	-1.94251565
H	-1.54656614	0.81111078	-1.53246567
H	2.52594130	0.41851978	-0.02536769
H	-2.40463653	0.41851978	0.77378688
H	1.61419865	0.02059278	2.19988868
H	-0.83669117	0.02059278	2.59713215

Transition state of cyclization from **1** to **3**

C	-1.46271978	0.00000000	-0.77904999
C	-0.97267397	0.92656214	0.27199165
C	-0.97267397	-0.92656214	0.27199165
C	0.34797021	1.44442973	0.25444240
C	0.34797021	-1.44442973	0.25444240
C	1.44491155	0.71033136	-0.13679094
C	1.44491155	-0.71033136	-0.13679094
H	-0.89768415	0.00000000	-1.70832657
H	-2.53781540	0.00000000	-0.93100326
H	-1.71660382	1.40292615	0.90135148
H	-1.71660382	-1.40292615	0.90135148
H	0.49864932	2.44603403	0.64636482
H	0.49864932	-2.44603403	0.64636482
H	2.40261685	1.21220510	-0.22876006
H	2.40261685	-1.21220510	-0.22876006

3,4-dimethylene-1,5-cycloheptadiene (**4**)

C	0.00000000	0.00000000	2.27769370
C	0.30757462	1.26922370	1.54466177
C	-0.30757462	-1.26922370	1.54466177
C	0.25520407	1.56914286	0.24132897
C	-0.25520407	-1.56914286	0.24132897
C	-0.08449230	0.74149911	-0.92616070
C	0.08449230	-0.74149911	-0.92616070
C	0.54024285	-1.36320023	-2.02983111
C	-0.54024285	1.36320023	-2.02983111
H	-0.83683843	0.21196005	2.96196991
H	0.83683843	-0.21196005	2.96196991
H	0.56455576	2.09014503	2.21089852
H	-0.56455576	-2.09014503	2.21089852

H	0.45500152	2.60658015	-0.01602313
H	-0.45500152	-2.60658015	-0.01602313
H	0.85761316	-0.81418222	-2.90669094
H	-0.85761316	0.81418222	-2.90669094
H	0.63055890	-2.44327000	-2.06322903
H	-0.63055890	2.44327000	-2.06322903

1,7-(3,7-norboano)cycloheptatriene (**11**)

C	0.39161107	-0.70780398	0.00000000
C	1.88954024	-0.52395157	0.00000000
C	-0.00026367	0.76765306	0.00000000
C	2.07670654	0.36971792	1.25405743
C	2.07670654	0.36971792	-1.25405743
C	0.79669589	1.26568549	-1.25305727
C	0.79669589	1.26568549	1.25305727
H	2.48815886	-1.43505798	0.00000000
H	2.99886930	0.95407799	1.19738001
H	2.12643255	-0.24107211	2.15811043
H	2.12643255	-0.24107211	-2.15811043
H	2.99886930	0.95407799	-1.19738001
H	0.20465857	1.10954860	-2.15709882
H	1.02337738	2.33328139	-1.18338471
H	0.20465857	1.10954860	2.15709882
H	1.02337738	2.33328139	1.18338471
C	-1.43874038	1.16985135	0.00000000
C	-0.31618984	-1.84434416	0.00000000
C	-2.55177995	0.41300817	0.00000000
C	-1.76193190	-1.99698539	0.00000000
C	-2.71007025	-1.03371431	0.00000000
H	0.24912941	-2.77413236	0.00000000
H	-2.11330718	-3.02508133	0.00000000
H	-3.74227958	-1.37228978	0.00000000
H	-3.49229582	0.95887051	0.00000000
H	-1.58996245	2.24889924	0.00000000

Structures of 7-X- cycloheptatrienes (presented in Table 1)

X=BH_2

C	-0.35872228	-1.14878488	-0.00000032
C	0.34230510	-0.60799365	1.22547120
C	0.34230533	-0.60799304	-1.22547144

C	0.36014796	0.70653179	1.52869228
C	0.36014825	0.70653255	-1.52869186
C	-0.12351226	1.77228321	0.68144862
C	-0.12351213	1.77228355	-0.68144776
H	-1.38893041	-0.71108416	-0.00000031
B	-0.78030307	-2.64384801	-0.00000073
H	0.83132350	-1.31229664	1.89253280
H	0.83132386	-1.31229570	-1.89253330
H	0.78982797	1.00864988	2.48091870
H	0.78982844	1.00865111	-2.48091805
H	-0.38756911	2.70227613	1.17794504
H	-0.38756889	2.70227671	-1.17794377
H	-0.98583981	-3.21204697	-1.02944573
H	-0.98584001	-3.21204748	1.02944394

X=CH_3

C	-0.41729640	-1.03751540	-0.00000004
C	0.32617075	-0.51722994	1.20668603
C	0.32617079	-0.51722985	-1.20668606
C	0.35469385	0.79483363	1.52314583
C	0.35469390	0.79483374	-1.52314576
C	-0.12698470	1.86475512	0.68233076
C	-0.12698468	1.86475517	-0.68233063
H	-1.41552996	-0.57737496	-0.00000004
C	-0.56925743	-2.55988516	-0.00000010
H	0.83304429	-1.23699302	1.84506084
H	0.83304435	-1.23699289	-1.84506090
H	0.80115727	1.08966446	2.46966593
H	0.80115735	1.08966464	-2.46966583
H	-0.37796699	2.79822298	1.17919910
H	-0.37796696	2.79822306	-1.17919890
H	-1.11626474	-2.89755506	-0.88429524
H	-1.11626477	-2.89755512	0.88429499
H	0.40835362	-3.05320789	-0.00000011

X=NH_2

C	-0.42062874	-1.04040014	0.00000000
C	0.33565463	-0.53922870	1.20168422
C	0.33565463	-0.53922870	-1.20168422

C	0.36008760	0.77172782	1.52295675
C	0.36008760	0.77172782	-1.52295675
C	-0.12647124	1.83952456	0.68300805
C	-0.12647124	1.83952456	-0.68300805
H	-1.41144029	-0.55492594	0.00000000
N	-0.49721114	-2.50503973	0.00000000
H	0.85732076	-1.27483624	1.80734180
H	0.85732076	-1.27483624	-1.80734180
H	0.81596522	1.06669092	2.46455720
H	0.81596522	1.06669092	-2.46455720
H	-0.37575626	2.77394984	1.17885903
H	-0.37575626	2.77394984	-1.17885903
H	-1.00531028	-2.83164407	-0.81619640
H	-1.00531028	-2.83164407	0.81619640

X=OH

C	-0.40802817	-1.07893673	0.00000003
C	0.29919017	-0.53789512	1.21849018
C	0.29919016	-0.53789519	-1.21849015
C	0.31411700	0.77367292	1.52761388
C	0.31411699	0.77367283	-1.52761393
C	-0.16832433	1.84097807	0.68125371
C	-0.16832433	1.84097803	-0.68125381
H	-1.44752318	-0.73036345	0.00000003
O	-0.49741565	-2.50045177	0.00000007
H	0.76757822	-1.26473924	1.87693083
H	0.76757821	-1.26473934	-1.87693076
H	0.73650197	1.07161427	2.48367236
H	0.73650195	1.07161413	-2.48367243
H	-0.43359005	2.76962989	1.17901138
H	-0.43359006	2.76962982	-1.17901154
H	0.39424322	-2.86648082	0.00000008

X=F

C	-0.40124393	-1.06225508	0.00000000
C	0.30759966	-0.55291354	1.21848293
C	0.30759966	-0.55291354	-1.21848293
C	0.31271075	0.75762714	1.52963616
C	0.31271075	0.75762714	-1.52963616
C	-0.18106740	1.81937547	0.68163840
C	-0.18106740	1.81937547	-0.68163840

H	-1.45255586	-0.74733665	0.00000000
F	-0.39691955	-2.46596287	0.00000000
H	0.79305272	-1.29275208	1.84625673
H	0.79305272	-1.29275208	-1.84625673
H	0.74137300	1.05915376	2.48130700
H	0.74137300	1.05915376	-2.48130700
H	-0.45373609	2.74633038	1.17833503
H	-0.45373609	2.74633038	-1.17833503

X=CN

C	-0.35605247	-0.75806582	-0.00000009
C	0.38977046	-0.26148565	1.22350074
C	0.38977061	-0.26148544	-1.22350073
C	0.40737034	1.05123723	1.52478661
C	0.40737052	1.05123749	-1.52478638
C	-0.09332242	2.11175388	0.68174096
C	-0.09332234	2.11175399	-0.68174061
H	-1.35862515	-0.30712001	-0.00000011
C	-0.52588286	-2.21109485	-0.00000022
H	0.88953013	-0.98844626	1.85340856
H	0.88953035	-0.98844595	-1.85340862
H	0.85617345	1.35225105	2.46752595
H	0.85617375	1.35225147	-2.46752561
H	-0.36529760	3.03822261	1.17944348
H	-0.36529745	3.03822281	-1.17944300
N	-0.65091408	-3.35714868	-0.00000033

X=CMe_3

C	-0.15925452	-0.10969180	0.00000000
C	0.61052415	0.38861557	1.20005594
C	0.61052404	0.38861558	-1.20005599
C	0.66138798	1.70076801	1.51715188
C	0.66138785	1.70076802	-1.51715192
C	0.19002202	2.77899440	0.68262729
C	0.19002196	2.77899440	-0.68262728
H	-1.12464329	0.41761022	0.00000005
C	-0.48154036	-1.63401188	0.00000002
H	1.12329260	-0.32749800	1.83452920
H	1.12329243	-0.32749798	-1.83452931
H	1.12464505	1.98748962	2.45823313
H	1.12464483	1.98748964	-2.45823322

H	-0.04547322	3.71569679	1.18104481
H	-0.04547333	3.71569680	-1.18104478
C	-1.32014624	-1.96483264	-1.25037175
C	-1.32014613	-1.96483265	1.25037186
C	0.79141098	-2.50313782	-0.00000005
H	-0.77083757	-1.76818584	-2.17476419
H	-0.77083737	-1.76818585	2.17476425
H	-2.23801935	-1.36937717	-1.27577675
H	-2.23801923	-1.36937718	1.27577694
H	-1.60556290	-3.02116104	-1.25201679
H	-1.60556278	-3.02116104	1.25201691
H	0.52181302	-3.56362117	-0.00000004
H	1.41079539	-2.32470645	0.88279710
H	1.41079531	-2.32470644	-0.88279724