

SUPPLEMENTAL INFORMATION

Theoretical Study of Cyclohexadiene/Hexatriene Photochemical Interconversion using Spin-Flip Time-Dependent Density Functional Theory Supplemental Information.

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ARTICLE HISTORY

Compiled April 28, 2020

The Cartesian geometry of critical points located on S₀, S₁ and S₂, and their nuclear repulsion energy are given below.

1,3-cyclohexadiene (CHD), S₀ optimized geometry. E_{NN}= 218.8618131564 hartrees

C	-2.0882581642	0.6374657635	0.0165109268
C	-3.3893732856	0.2837169778	-0.6596225929
C	-3.3864662267	0.6812905712	-2.1386667717
C	-2.0851341215	0.3215060189	-2.8112043523
H	-2.0819902600	0.1231744987	-3.8859832626
C	-0.9397734672	0.3198216228	-2.1133706351
H	0.0122699402	0.1069907862	-2.6047562036
C	-0.9409914876	0.6338150516	-0.6781727447
H	0.0107137604	0.8420175373	-0.1841571964
H	-2.0871718305	0.8357317736	1.0913053062
H	-4.2399955859	0.7531168386	-0.1433029371
H	-3.5386927882	-0.8105763641	-0.5682384784
H	-4.2377887049	0.2156412090	-2.6572293576
H	-3.5306194784	1.7762345149	-2.2305195007

all-cis-hexatriene (cZc-HT), S₀ optimized geometry. E_{NN}= 203.5325477739 hartrees

C	-2.0036226284	0.5746825143	0.5564564115
C	1.1841528775	1.0138372001	-0.6688745992
H	1.1277672962	1.1087799408	0.4182768057
C	0.7862094245	-0.0971896737	-1.2939276997
H	0.8940696881	-0.1535135359	-2.3837439115
C	0.2889045261	-1.3277419966	-0.6514292472
H	0.6915595490	-2.2521809111	-1.0812958404
C	-0.5657094359	-1.4711763121	0.3760265357

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H	-0.7276603800	-2.4945731807	0.7340269446
C	-1.3410392291	-0.4483916817	1.1021507503
H	-1.4229201116	-0.6086959227	2.1838826247
H	1.5754727958	1.8651014850	-1.2297549385
H	-1.9821951572	0.7596639506	-0.5201930379
H	-2.5871592151	1.2593581235	1.1753892018

CHD-S1min, S1 optimized geometry. E_NN= 216.0185526817 hartrees

C	-2.1070360651	0.6688699505	0.0952464357
C	-3.2293257411	0.0314004186	-0.4585915429
C	-3.4245704057	0.9433597700	-2.4078774699
C	-2.2297990461	0.2988035799	-2.7303657811
H	-2.2468055038	-0.2954276527	-3.6466817425
C	-1.0012477155	0.2554941218	-2.0166511572
H	-0.1117596086	-0.0682565128	-2.5417413246
C	-0.9417589091	0.6390642218	-0.6800163750
H	0.0130407033	0.9202348193	-0.2376123623
H	-2.2198649417	1.3628043794	0.9200000733
H	-4.2272198273	0.2625620980	-0.0997462619
H	-3.1104734752	-0.9690481562	-0.8622418151
H	-4.2560892929	0.8269543587	-3.0944308529
H	-3.4303618713	1.8431314038	-1.8066976239

CHD-S2min, S2 optimized geometry. E_NN= 213.9569528972 hartrees

C	-2.1545960349	0.6585702298	0.0593611608
C	-3.3485863038	0.0664901213	-0.3636585144
C	-3.3444756991	0.8967010622	-2.4351047874
C	-2.1513511908	0.2998590154	-2.8536967422
H	-2.1477546326	-0.2793786374	-3.7745618614
C	-0.9792311944	0.3181331426	-2.0768052459
H	-0.0351718333	0.0684467465	-2.5523448618
C	-0.9805782792	0.6388992147	-0.7145269492
H	-0.0371060252	0.8858472495	-0.2364735687
H	-2.1522171287	1.2371726214	0.9806047419
H	-4.2686017218	0.2948207794	0.1665239295
H	-3.3330742715	-0.8919918617	-0.8680644319
H	-4.2640903635	0.6706483314	-2.9668925759
H	-3.3264370213	1.8557287848	-1.9317680934

CI-S2/S1, MECP-S2/S1 optimized geometry. E_NN= 214.3327014884 hartrees

C	-2.1600874578	0.6259319373	0.0483277217
C	-3.3625285054	0.0850627788	-0.4653782806
C	-3.3583440563	0.8797365490	-2.3328497028
C	-2.1567840489	0.3333623069	-2.8429414771
H	-2.1956270151	-0.3753643020	-3.6683848986
C	-0.9263437294	0.4032635722	-2.0781556548
H	0.0220427073	0.2932788349	-2.5954107813
C	-0.9279374630	0.5502104512	-0.7132919056

H	0.0197789190	0.6554918828	-0.1934576392
H	-2.1979518488	1.3351783094	0.8731634618
H	-4.2889894267	0.3616260155	0.0321744148
H	-3.3568912200	-0.9382767545	-0.8299751641
H	-4.2845572837	0.6075039261	-2.8330882219
H	-3.3490512712	1.9029412925	-1.9681396726

CI'-S2/S1, MECP-S2/S1 optimized geometry. E_NN= 212.2485409604 hartrees

C	-2.1428856174	0.6630139022	0.0817964702
C	-3.3538372570	0.0509096859	-0.2983563073
C	-3.3488465640	0.9137235658	-2.4993113468
C	-2.1393864627	0.2960022012	-2.8766370887
H	-2.1048037561	-0.2393254109	-3.8227201097
C	-0.9991650244	0.2863210790	-2.0783703127
H	-0.0578028504	-0.0223790844	-2.5245696072
C	-1.0002996058	0.6672100840	-0.7132679306
H	-0.0589628938	0.9723808710	-0.2649130523
H	-2.1082268753	1.1976497383	1.0282548820
H	-4.2624538697	0.2726815505	0.2517716233
H	-3.3493186757	-0.8782699266	-0.8536716198
H	-4.2567577359	0.6969103094	-3.0530480656
H	-3.3405245119	1.8431182346	-1.9443653348

CI-S1/S0, MECP-S1/S0 optimized geometry. E_NN= 216.8012376711 hartrees

C	-2.2502643848	0.6808921738	-0.1051889799
C	-3.4324363404	-0.0023768797	-0.3899361933
C	-3.1999439186	0.9341338374	-2.3026710644
C	-2.0956536687	0.2881586508	-2.8859483918
H	-2.2390826953	-0.4117738461	-3.7006511114
C	-0.9290922973	0.2913490216	-2.1142187838
H	0.0231641280	-0.0031226106	-2.5530023970
C	-0.9990718999	0.6827895804	-0.7821441364
H	-0.1240830253	1.0340912319	-0.2506447372
H	-2.2996437533	1.3465980986	0.7602460337
H	-4.2692078311	0.1446977541	0.2830158659
H	-3.4311635423	-0.9164722433	-0.9680604274
H	-4.2086893633	0.7061620600	-2.6323047152
H	-3.0681031078	1.9448199712	-1.9258987620

TS-S0, Transition state geometry. E_NN= 217.63841635 hartrees

C	-1.3703302	0.6985916	0.2115755
C	0.5402839	0.9555572	-0.3208925
H	0.8489557	0.9487921	0.7150975
C	0.7029190	-0.1397923	-1.1106276
H	0.5749651	-0.0244070	-2.1862328
C	0.3927670	-1.4815145	-0.5722787
H	0.9062961	-2.3566174	-0.9589144
C	-0.6297433	-1.6395173	0.2857584

H	-0.9161831	-2.6393535	0.5978708
C	-1.2497559	-0.4562224	0.9196373
H	-1.1381139	-0.3891642	2.0011225
H	0.5439900	1.9425683	-0.7783869
H	-1.6782025	0.6890599	-0.8246522
H	-1.6100179	1.6199796	0.7379131

The state-averaged Natural Transition Orbitals (NTOs) involved in the transitions are shown in Figure 1.

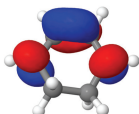
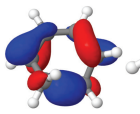
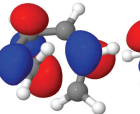
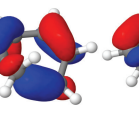
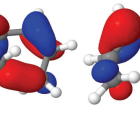
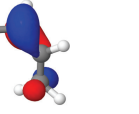
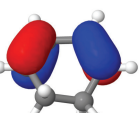
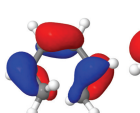
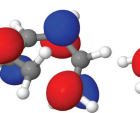
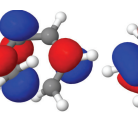
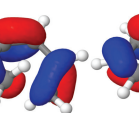
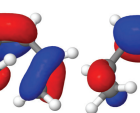
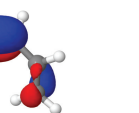
Particle:							
Symmetry of particle:	C₂(B)	C₂(A)	C₁(A)	C₁(A)	C₂(A)	C₂(A)	C₂(A)
Hole:							
Symmetry of hole:	C₂(A)	C₂(B)	C₁(A)	C₁(A)	C₂(B)	C₂(B)	C₂(B)
Direct product:	AxB = B	BxA = B	AxA = A	AxA = A	BxA = B	BxA = B	BxA = B
Symmetry of product:	C₂(B)	C₂(B)	C₁(A)	C₁(A)	C₂(B)	C₂(B)	C₂(B)
Critical point:	S₁(CHD) 1.53 Å	CI_{S2/S1} 2.03 Å	CI_{S1/S0} 2.14 Å	S_{1min} 2.16 Å	S_{2min} 2.23 Å	CI'_{S2/S1} 2.36 Å	S₁(cZc-HT) 3.44 Å

Figure 1. NTOs, symmetries and irreducible representations of all critical points. The symmetry of each critical point is generated by the direct product between the irreducible representation of the hole and particle NTOs.