SUPPORTING INFORMATION

Understanding the Mechanism of Non-Polar Diels-Alder Reactions. A Comparative ELF Analysis of Concerted and Stepwise Diradical Mechanisms.

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- **SI3** Complete citation for reference 19.
- SI4 B3LYP/6-31G* computed total energies, unique frequency imaginary, and cartesian coordinates of the stationary points involved in the non-polar Diels-Alder reactions of cyclopentadiene 1 with ethylene 2 and styrene 10.

Complete citation for reference 19.

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.;

Cheeseman, J. R.; Montgomery, J., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.;

Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.;

Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.;

Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.;

Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.;

Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A.

J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth,

G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels,

A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.;

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Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.;

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B3LYP/6-31G* computed total energies, unique frequency imaginary, and cartesian coordinates of the stationary points involved in the non-polar Diels-Alder reactions of cyclopentadiene 1 with ethylene 2 and styrene 10.

1 E(RB+HF-LYP) = -194.101058523 A.U.

С	1.17609500	-0.30213700	-0.0000300
С	0.75209500	0.97843500	0.00000100
С	-0.71768200	1.00389000	-0.0000300
С	-1.18580400	-0.26122000	0.00000200
Н	2.20304700	-0.64929100	-0.0000300
Н	1.37992200	1.86378700	0.00000900
Н	-1.31437900	1.91048100	-0.00000200
Н	-2.22426000	-0.57233200	-0.00000200
С	-0.02121700	-1.21720800	0.00000100
Н	-0.03262000	-1.88160200	0.87801400
Н	-0.03262800	-1.88160300	-0.87801100

2

E(RB+HF-LYP) = -78.5874572173 A.U.

С	0.0000000	0.66530700	0.0000000
С	0.0000000	-0.66530700	0.0000000
Н	-0.92290200	1.24056600	0.0000000
Н	0.92290300	1.24056600	0.0000000
Н	0.92290200	-1.24056600	0.0000000
Н	-0.92290300	-1.24056600	0.0000000

TS1c

E(RB+HF-LYP) = -272.656773621 A.U.

1 imaginary frequencies -498.4451 cm-1

С	0.46049100	-1.15745600	0.35840900
С	1.18974900	-0.70277100	-0.74441600
С	1.18975700	0.70300800	-0.74426600
С	0.46018400	1.15742900	0.35849300
С	-1.62905500	-0.69401500	-0.33210200
С	0.37699600	-0.00010000	1.32642500
С	-1.62905500	0.69393200	-0.33196200
Н	0.40706900	2.19542800	0.67196800

Н	1.57386600	1.32899600	-1.54363600
Н	1.57392100	-1.32860000	-1.54387700
Н	0.40748200	-2.19549700	0.67171400
Н	-1.56736100	-1.24390200	-1.26470700
Н	-2.07733300	-1.24135100	0.49233500
Н	-1.56746400	1.24397600	-1.26448500
Н	-2.07746200	1.24106300	0.49254500
Н	1.29332600	-0.00002900	1.94209500
Н	-0.48044900	-0.00025600	2.00256600

TS11

E(UB+HF-LYP) = -272.633098009 A.U. 1 imaginary frequencies -774.4682 cm-1

C	-0.14808400	-0.18289700	0.71050600
С	0.43763400	1.11211000	0.49690500
С	1.61340700	0.99272500	-0.28676100
C	1.92275600	-0.33082700	-0.48101900
Н	-0.01452100	2.05003500	0.80087300
Н	2.17617100	1.83292200	-0.68287200
Н	2.73547500	-0.72380000	-1.08106200
С	0.94812200	-1.18114500	0.28932800
Н	1.42617500	-1.57958800	1.19904800
Н	0.58219300	-2.04893200	-0.27204300
Н	-0.65849500	-0.37956700	1.65113600
С	-1.57149400	-0.46561500	-0.47958400
Н	-1.68340600	-1.54084200	-0.32949200
Н	-1.03574200	-0.24036700	-1.40383100
С	-2.73569800	0.28711400	-0.21671100
Н	-2.82960800	1.31903700	-0.54361400
Н	-3.49809700	-0.07769300	0.46586900

DR1

E(UB+HF-LYP) = -272.642138326 A.U.

С	-0.26146400	-0.24202400	0.49869800
С	0.32994400	1.12791700	0.28937800
С	1.64227500	1.03534900	-0.16220900
С	2.04517700	-0.28968000	-0.26134700
Н	-0.22227600	2.04804300	0.44569000
Н	2.26757100	1.88840700	-0.41109200
Н	3.01284800	-0.63641100	-0.60739300
С	0.93024600	-1.20423500	0.17722700
Н	1.21425100	-1.79640100	1.05977100
Н	0.66509300	-1.93492000	-0.60130400
Н	-0.59120700	-0.37156000	1.53925900

C	-1.51837200	-0.52493800	-0.40578900
Н	-1.77983000	-1.58340400	-0.26832600
Н	-1.20345700	-0.40272100	-1.45075400
С	-2.69636800	0.33165800	-0.10874600
Н	-2.80123200	1.31659000	-0.55326900
Н	-3.39038800	0.06808900	0.68413700

3

E(RB+HF-LYP) = -272.727426153 A.U.

C	-0.08823100	1.12825100	0.32340800
С	-1.27893000	0.67026000	-0.50785600
C	-1.27893800	-0.67026600	-0.50805500
C	-0.08774200	-1.12855900	0.32252600
C	1.19121300	0.78118000	-0.51588500
С	-0.04175400	-0.00059300	1.38055200
C	1.19183900	-0.78030700	-0.51623900
Н	-0.11965000	-2.15779200	0.68869900
Н	-1.92004800	-1.32868500	-1.08653100
Н	-1.92077200	1.32869200	-1.08551900
Н	-0.12005600	2.15729300	0.69019600
Н	2.08847300	1.17874400	-0.02764800
Н	1.14808400	-1.20633800	-1.52300600
Н	-0.91317400	-0.00092300	2.04290300
Н	0.87747600	-0.00065700	1.97994100
Н	2.08892100	-1.17708300	-0.02706400
Н	1.14600300	1.20695400	-1.52267300

10

E(RB+HF-LYP) = -309.648258763 A.U.

C	-1.36244700	1.32938500	-0.00028800
C	0.00874300	1.09279600	-0.00128500
C	0.51522500	-0.22011900	-0.00102800
С	-0.40629900	-1.28118900	-0.00012200
C	-1.78074700	-1.04633400	0.00086300
C	-2.26540200	0.26155900	0.00089600
Н	-1.73082500	2.35204800	-0.00085500
Н	0.69369300	1.93578700	-0.00305400
Н	-0.03460800	-2.30357200	0.00004600
Н	-2.47173700	-1.88527300	0.00152000
Н	-3.33553400	0.45016800	0.00155800
С	1.95465400	-0.52919700	-0.00130700
С	2.97753300	0.33479000	0.00187400
Н	2.18588000	-1.59464000	-0.00412400
Н	4.00446700	-0.01754600	0.00150600

Η

2.84111500 1.41288100 0.00578000

TS2c E(RB+HF-LYP) = -503.716310090 A.U. 1 imaginary frequencies -464.1932 cm-1

С	1.70290100	-0.71522400	-1.24203200
С	1.41214800	0.62561100	-1.44649800
С	2.09013700	1.39916300	-0.48580000
С	2.76020200	0.53176600	0.40237600
С	0.38771100	-0.89143400	0.90981700
С	2.90085100	-0.78977800	-0.33529700
С	1.30652300	-0.14612200	1.66207200
Н	3.52337800	0.88026900	1.09397900
Н	1.98740200	2.47164000	-0.35690600
Н	0.69434400	1.01017400	-2.16294500
Н	1.35374400	-1.53613000	-1.85833700
Н	0.53413600	-1.96615200	0.84055100
Н	0.98942400	0.79609400	2.09887800
Н	3.81739200	-0.74299200	-0.94907900
Н	2.96956900	-1.68050600	0.29347000
Н	1.99636200	-0.69672100	2.29663500
С	-0.92591600	-0.41209800	0.48620500
С	-1.31165900	0.94172400	0.57195600
С	-1.87012400	-1.32503900	-0.02947900
С	-2.57414500	1.35808300	0.15265200
Н	-0.61842800	1.67599400	0.97044000
С	-3.13249900	-0.90985300	-0.43988000
Н	-1.59803000	-2.37599800	-0.10475000
С	-3.49397000	0.43821600	-0.35429700
Н	-2.84319500	2.40894400	0.22900000
Н	-3.83895100	-1.63937000	-0.82850700
Н	-4.48009600	0.76467200	-0.67319400

TS21

E(UB+HF-LYP) = -503.704339099 A.U. 1 imaginary frequencies -800.7672 cm-1

С	0.0000000	0.0000000	0.0000000
С	0.0000000	0.0000000	1.42702900
С	1.33481800	0.0000000	1.91951600
С	2.22039900	-0.13403800	0.88317800
Н	-0.88918000	0.07456600	2.04388100
Н	1.60301600	0.10379900	2.96665600
Н	3.30215500	-0.11699100	0.94913100

C	1.45224700	-0.31439300	-0.39847600
Н	1.50294000	-1.36455700	-0.72926500
Н	1.84054400	0.28732700	-1.22884200
Н	-0.79469800	-0.51318300	-0.53838500
C	-0.36294800	1.76006700	-0.67801000
Н	-0.01884500	1.57354500	-1.69458100
Н	0.37025100	2.31595500	-0.09560800
C	-1.71073700	2.15317100	-0.53779500
Н	-2.00082600	2.64248000	0.39122600
С	-2.78859900	1.82843700	-1.43273600
C	-4.10931500	2.23594300	-1.11452800
С	-2.61113400	1.10021800	-2.63722000
C	-5.18167300	1.93984300	-1.94616400
Н	-4.27582600	2.79420000	-0.19579600
С	-3.68856000	0.80160800	-3.46306500
Н	-1.61739700	0.76857800	-2.92443900
С	-4.98162300	1.21791500	-3.12797600
Н	-6.18116200	2.26921500	-1.67304700
Н	-3.52093600	0.23985700	-4.37884600
Н	-5.81989900	0.98386400	-3.77819600

DR2

E(UB+HF-LYP) = -503.717227034 A.U.

С	1.84634100	0.28300800	-0.18220800
С	2.49271000	-0.99989200	-0.63966200
С	3.87881300	-0.89229200	-0.61115900
С	4.27455700	0.36996800	-0.18911800
Н	1.93201800	-1.88030600	-0.93385300
Н	4.56220100	-1.69309400	-0.87990600
Н	5.29763800	0.70739200	-0.06379000
С	3.06569800	1.22493000	0.09275800
Н	3.03664600	2.11668900	-0.55045400
Н	3.06222900	1.60171400	1.12672800
Н	1.21040700	0.69947600	-0.97664000
С	0.92597900	0.11083500	1.07644600
Н	0.62253800	1.11368000	1.40354200
Н	1.54046400	-0.31064200	1.88230400
С	-0.26812500	-0.75640800	0.84710300
Н	-0.13904100	-1.82720100	0.99410800
С	-1.53545900	-0.32558100	0.38245100
С	-2.57704500	-1.27851800	0.17508800
С	-1.84451500	1.03789500	0.10086200
С	-3.82975200	-0.89610000	-0.27664100
Н	-2.37087800	-2.32632500	0.38160100
С	-3.10199600	1.40983400	-0.35323900
Н	-1.08400300	1.79975300	0.24249400

С	-4.10595200	0.45204200	-0.54625900
Н	-4.60175300	-1.64739600	-0.42318600
Н	-3.30770800	2.45713000	-0.56057300
Н	-5.08828700	0.75080600	-0.90090400

11

E(RB+HF-LYP) = -503.776345181 A.U.

С	1.42883400	-0.66329700	-0.94772600
С	1.54446600	0.81836100	-1.26945200
С	2.32439700	1.37418600	-0.33086300
С	2.72851900	0.27330100	0.63825000
С	0.53891800	-0.81335600	0.35824200
С	2.82585800	-0.92292800	-0.33735700
С	1.43164300	-0.11031500	1.43596300
Н	3.59719500	0.47858800	1.26885400
Н	2.53950800	2.42987200	-0.19450000
Н	0.99592500	1.32669400	-2.05529200
Н	1.10461500	-1.31226900	-1.76474000
Н	0.50810700	-1.88641500	0.58251900
Н	0.95235900	0.76463900	1.88303400
Н	3.63514400	-0.81322200	-1.06613800
Н	2.91086200	-1.89475100	0.16486400
Н	1.66842600	-0.80291500	2.25176200
С	-0.89866000	-0.35252700	0.21837000
С	-1.28679900	0.99274800	0.31399900
С	-1.89635500	-1.30280200	-0.04855800
С	-2.61971800	1.37059300	0.14360600
Н	-0.54191800	1.75483700	0.51912600
С	-3.22975500	-0.93073800	-0.21990000
Н	-1.62057800	-2.35323700	-0.11992800
С	-3.59786300	0.41201400	-0.12452400
Н	-2.89401500	2.41957900	0.22483300
Н	-3.98062200	-1.69038800	-0.42251400
Н	-4.63592700	0.70755300	-0.25218500