ELECTRONIC SUPPLEMENTARY INFORMATION FOR:

On the origin of the alternating Diels–Alder reactivity in [*n*]dendralenes

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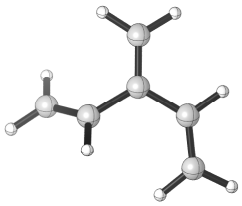
1. Computational Methods

All calculations were carried out using GAUSSIAN 09.[1] All calculations were gas phase ones. The G4(MP2) method was used throughout to calculate the free energies presented in this paper.[2] The G4(MP2) method uses B3LYP/6-31G(2df,p) optimised geometries to calculate vibrational frequencies and thermal corrections. Care was taken to verify that all computed TSs possessed a single negative eigenvalue of the Hessian matrix. Free energies refer to a standard state of an ideal gas at 1 atm and 298.25 K. The restricted formalism was used for all calculations reported here. The validity of this stratagem was validated by carrying out stability calculations on the B3LYP/6-31G(2df,p) Kohn-Sham determinant for every molecular system studied and it was verified that the KS determinant was stable with respect to the RKS→UKS perturbation. In particular, all bis-pericyclic TS restricted closed-shell B3LYP/6-31G(2df) KS determinants were found to be stable.

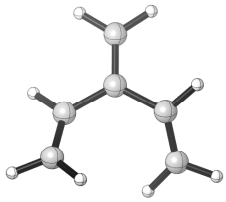
1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09*, Revision A.1: Gaussian, Inc., Wallingford CT, 2009.

2 L. A. Curtiss, P. C. Redfern and K. Raghavachari, *J. Chem. Phys.*, 2007, **127**, 124105/1–8.

2. Structures and Relative Enthalpies of [3]Dendralenes and [4]Dendralenes



cis, trans-[3]dendralene



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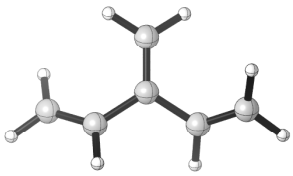
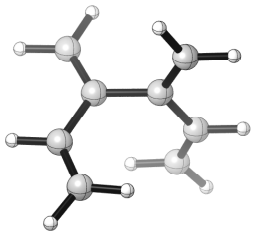


cis, cis-[3]dendralene

H_{rel} (kJ.mol) 298 K

0.0 **3.7** **10.2**



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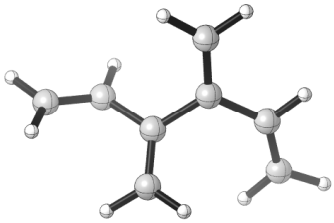
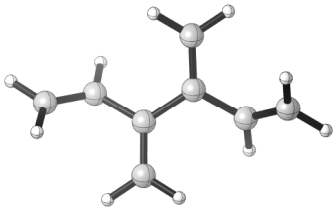


ctt-[4]dendralene

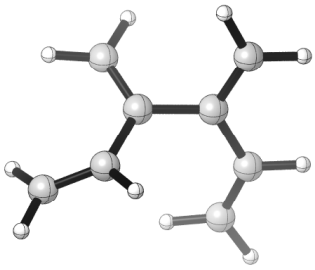


ctc-[4]dendralene

H_{rel} (kJ.mol) 298 K

0.0 **12.8** **12.2**

cct-[4]dendralene



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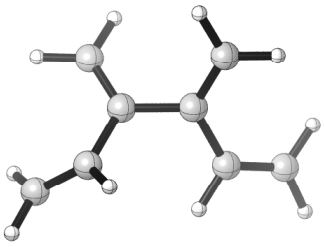

10.1 **20.8**

3. Cartesian Coordinates and Energies of [3]Dendralene Conformers

Three stable conformers of [3]dendralene were located. The Cartesian coordinates and energies of the conformations are:

cis_trans_3_DendraleneG4MP2
g4mp2
Energy (0K) = -232.990491 au
Enthalpy (298K) = -232.982890 au; Gibbs free energy (298K) = -233.020573 au

C	2.064582	-0.899996	-0.114193
C	1.444242	0.280254	-0.040251
H	1.525026	-1.840655	-0.092786
H	3.142647	-0.963442	-0.210224
H	2.038968	1.190761	-0.086562
C	-0.002233	0.494196	0.091607
C	-0.503983	1.739431	0.031117
H	-1.560812	1.934099	0.170034
H	0.136459	2.596439	-0.150786
C	-0.873770	-0.677055	0.320923
C	-2.069637	-0.867064	-0.235335
H	-0.481224	-1.433288	0.998315
H	-2.671312	-1.738659	-0.000930
H	-2.484956	-0.163856	-0.950263

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trans_trans_3_DendraleneG4MP2
g4mp2
Energy (0K) = -232.989064 au
Enthalpy (298K) = -232.981483 au; Gibbs free energy (298K) = -233.019046 au

C	-1.591869	-1.266698	0.202882
C	-1.282885	-0.022896	-0.170430
H	-0.880204	-1.927955	0.681423
H	-2.595730	-1.652528	0.062178
H	-2.069721	0.591394	-0.605223
C	-0.000078	0.681410	-0.000117
C	-0.000339	2.027688	-0.000029
H	0.910844	2.596425	0.150393
H	-0.911745	2.596099	-0.150331
C	1.282972	-0.022421	0.170098
C	1.592191	-1.266394	-0.202464
H	2.069811	0.592417	0.604114
H	2.596246	-1.651779	-0.061934
H	0.880546	-1.928212	-0.680257

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cis_cis_3_DendraleneG4MP2
g4mp2
Energy (0K) = -232.986777 au

Enthalpy (298K) = -232.979020 au; Gibbs free energy (298K) = -233.017183 au

C	-2.463331	-0.267503	-0.105116
C	-1.225935	-0.617205	0.247909
H	-2.664857	0.651344	-0.646726
H	-3.317107	-0.894094	0.128615
H	-1.073844	-1.575378	0.743406
C	0.000002	0.170397	0.000100
C	-0.000005	1.512479	0.000080
H	0.889167	2.078130	-0.253837
H	-0.889202	2.078098	0.253971
C	1.225868	-0.617306	-0.247682
C	2.463400	-0.267486	0.104761
H	1.073606	-1.575717	-0.742665
H	3.317058	-0.894243	-0.128954
H	2.665183	0.651598	0.645873

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4. Cartesian Coordinates and Energies of [4]Dendralene Conformers

Five conformers of [4]dendralene were calculated. Their Cartesian coordinates and energies are:

tct_4_Dendralene_G4MP2
g4mp2
Energy (0K) = -310.266069 au
Enthalpy (298K) = -310.256209 au; Gibbs free energy (298K) = -310.299157 au

C	-0.524750	1.796010	-1.377405
C	0.454449	1.608214	-0.489707
H	-1.378656	1.130501	-1.438759
H	-0.501977	2.628227	-2.071930
H	1.287137	2.309360	-0.462157
C	0.524750	0.534906	0.507656
C	1.506442	0.518495	1.420267
H	1.574998	-0.262263	2.168689
H	2.270104	1.290353	1.439294
C	-0.524750	-0.534906	0.507656
C	-1.506442	-0.518495	1.420267
H	-2.270104	-1.290353	1.439294
H	-1.574998	0.262263	2.168689
C	-0.454449	-1.608214	-0.489707
C	0.524750	-1.796010	-1.377405
H	-1.287137	-2.309360	-0.462157
H	0.501977	-2.628227	-2.071930
H	1.378656	-1.130501	-1.438759

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cct_4_Dendralene_G4MP2
g4mp2
Energy (0K) = -310.262153 au

Enthalpy (298K) = -310.252351 au; Gibbs free energy (298K) = -310.295625 au

C	-2.600596	0.635142	-0.302465
C	-1.373250	0.272721	-0.680494
H	-3.013019	0.349586	0.660196
H	-3.232742	1.239703	-0.943441
H	-0.990953	0.632290	-1.633972
C	-0.446347	-0.586020	0.086637
C	-0.876303	-1.545111	0.917615
H	-0.180790	-2.141006	1.496998
H	-1.932781	-1.760710	1.036262
C	1.016153	-0.390577	-0.151569
C	1.775574	-1.421194	-0.556511
H	2.840665	-1.301766	-0.730369
H	1.352841	-2.403539	-0.729739
C	1.623314	0.930846	0.044798
C	1.033529	2.010853	0.564042
H	2.668253	0.996489	-0.254203
H	1.577389	2.941824	0.680506
H	-0.001305	2.007170	0.885447

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ctc_4_Dendralene_G4MP2

g4mp2

Energy (0K) = -310.261238 au

Enthalpy (298K) = -310.251548 au; Gibbs free energy (298K) = -310.294567 au

C	0.669364	1.707646	0.059756
C	0.639920	0.376413	-0.115431
H	-0.230502	2.277861	0.258744
H	1.601887	2.258054	0.014493
C	-0.639925	-0.376466	-0.115280
C	-0.669380	-1.707636	0.060380
H	-1.601915	-2.258044	0.015355
H	0.230480	-2.277798	0.259545
C	-1.888534	0.384853	-0.334995
C	-3.031127	0.194993	0.324689
H	-1.840527	1.161091	-1.096604
H	-3.922040	0.767827	0.090459
H	-3.113402	-0.532783	1.125702
C	1.888519	-0.384978	-0.334930
C	3.031161	-0.194852	0.324595
H	1.840473	-1.161513	-1.096234
H	3.922059	-0.767770	0.090516
H	3.113498	0.533238	1.125317

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ctt_4_Dendralene_G4MP2

g4mp2

Energy (0K) = -310.261025 au

Enthalpy (298K) = -310.251332 au; Gibbs free energy (298K) = -310.294355 au

C	-0.404265	1.960840	-0.354540
C	-0.658358	0.656071	-0.152041
H	0.605410	2.332756	-0.483648
H	-1.206675	2.689484	-0.404484
C	0.473042	-0.316368	-0.102247
C	0.399775	-1.534209	-0.659010
H	1.232508	-2.225878	-0.597162
H	-0.480293	-1.866114	-1.195667
C	1.704972	0.145005	0.572440
C	2.950406	-0.097120	0.161314
H	1.549767	0.750852	1.463460
H	3.809484	0.253569	0.723034
H	3.153949	-0.644968	-0.753243
C	-2.052546	0.225897	0.035076
C	-2.495535	-0.942868	0.504588
H	-2.785027	0.994892	-0.205804
H	-3.557643	-1.122271	0.630600
H	-1.826421	-1.745816	0.789441

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ccc_4_Dendralene_G4MP2

g4mp2

Energy (0K) = -310.258180 au

Enthalpy (298K) = -310.248276 au; Gibbs free energy (298K) = -310.292005 au

C	-2.656510	-1.109156	0.001644
C	-1.563972	-0.582418	0.556109
H	-2.997050	-0.807304	-0.983744
H	-3.243305	-1.864568	0.512966
H	-1.234552	-0.954730	1.525580
C	-0.724635	0.479362	-0.038406
C	-1.251091	1.494007	-0.737053
H	-0.621736	2.237926	-1.211946
H	-2.324128	1.606522	-0.846780
C	0.747241	0.383375	0.196800
C	1.438041	1.434924	0.659288
H	2.500624	1.369345	0.866736
H	0.950904	2.381373	0.862257
C	1.371828	-0.927467	-0.073386
C	2.627726	-1.129682	-0.474188
H	0.713805	-1.787698	0.032732
H	3.009554	-2.129833	-0.646914
H	3.314115	-0.308696	-0.655740

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5. Cartesian Coordinates and Energy of *N*-Methyl Maleimide

NMe_Maleimide_G4MP2
Reaction 1 N-MethylMaleimide1
g4mp2
Energy (0K) = -398.240422 au
Enthalpy (298K) = -398.232213 au; Gibbs free energy (298K) = -398.272595 au

C	-0.651639	-1.632118	0.000019
C	0.680912	-1.619568	0.000039
C	-1.146506	-0.212403	0.000022
C	1.150554	-0.191774	0.000031
O	2.284203	0.222396	-0.000125
O	-2.285623	0.186752	-0.000108
H	1.378479	-2.444805	0.000094
N	-0.006516	0.589955	0.000146
C	-0.022249	2.038858	0.000029
H	-0.532541	2.419253	0.888952
H	1.014873	2.376609	-0.002626
H	-0.537138	2.418773	-0.886418
H	-1.333140	-2.470667	0.000009

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6. Cartesian Coordinates and Energies of TSs for Addition of *N*-Methyl Maleimide (NMM) to [3]Dendralene

Four transition structures were calculated, distinguished by whether docking of NMM is exo (X) or endo (N) and whether the spectator vinyl group is *s-cisoid*-like or *s-transoid*-like.

ENDO addition of_NMM to 3_Dend_conf_1_G4MP2
Reaction 1 NMM_[3]Dendralene_DA2
G4MP2
Energy (0K) = -631.217171 au
Enthalpy (298K) = -631.202326 au; Gibbs free energy (298K) = -631.257825 au

C	0.374027	2.589379	-0.332667
C	-0.573390	1.822356	-0.955624
C	-1.519502	1.017072	-0.268923
C	-1.510274	1.008106	1.123862
C	0.432600	0.190214	1.648342
C	1.459602	0.861369	0.996385
C	0.236725	-1.124707	0.952303
C	1.898760	0.044034	-0.161871
O	2.792386	0.237845	-0.954268
O	-0.476830	-2.052271	1.261369
H	0.233407	2.976157	0.667552
H	1.168555	3.052808	-0.906273
H	-0.480824	1.666765	-2.027949
H	-2.170598	0.343570	1.668477

H	-1.229850	1.904849	1.660520
H	0.195370	0.276615	2.699688
H	2.095448	1.634262	1.400060
C	-2.307909	0.072359	-1.070723
C	-3.003475	-0.984041	-0.639118
H	-2.289294	0.274843	-2.140397
H	-3.542705	-1.613974	-1.337490
H	-3.044067	-1.278037	0.403242
N	1.055812	-1.083808	-0.170270
C	1.128785	-2.146521	-1.150867
H	1.894592	-1.869426	-1.876443
H	1.395730	-3.093292	-0.673041
H	0.163408	-2.270802	-1.649459

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ENDO addition of_NMM. 3_Dend_conf_2_G4MP2
G4MP2
Energy (0K) = -631.217606 au
Enthalpy (298K) = -631.202782 au; Gibbs free energy (298K) = -631.258369 au

C	-0.354361	2.444288	-0.443155
C	-1.178782	1.397732	-0.766959
C	-1.726523	0.512774	0.194190
C	-1.398105	0.685383	1.539728
C	0.736310	0.399349	1.605740
C	1.380408	1.235066	0.699054
C	0.743642	-0.986258	1.027526
C	1.769629	0.434564	-0.488819
O	2.400282	0.759221	-1.468932
O	0.373747	-2.023493	1.529362
H	-0.403611	2.937118	0.518790
H	0.171553	2.987160	-1.220218
H	-1.245547	1.106697	-1.810777
H	-1.731526	-0.051524	2.263187
H	-1.243922	1.678918	1.940019
H	0.732816	0.526768	2.679464
H	1.862683	2.177223	0.910853
C	-2.420328	-0.715916	-0.209933
C	-3.017716	-0.943361	-1.383340
H	-2.452980	-1.490574	0.553226
H	-3.518882	-1.883686	-1.581813
H	-3.051725	-0.202496	-2.175536
N	1.264559	-0.858174	-0.256209
C	1.391878	-1.958558	-1.188878
H	2.032110	-1.623373	-2.005921
H	1.836168	-2.823098	-0.689843
H	0.412412	-2.248127	-1.582343

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EXO addition of _NMM to 3_Dend_conf_1_G4MP2
Reaction 1 NMM_[3]Dendralene_DA3
G4MP2
Energy (0K) = -631.211591 au
Enthalpy (298K) = -631.196464 au; Gibbs free energy (298K) = -631.253826 au

C	-1.319742	-0.663249	-0.707897
C	-2.261493	0.314446	-0.401975
C	-1.861262	1.676895	-0.388710
C	-0.594974	2.108244	-0.675443
C	0.583918	0.814035	1.037183
C	0.107486	-0.485741	0.926991
C	1.928786	0.881099	0.409947
C	1.187937	-1.305861	0.274093
O	1.217706	-2.498597	0.078208
O	2.692232	1.815998	0.324739
H	-0.531706	-0.444254	-1.417081
H	-1.563943	-1.715911	-0.626331
H	-2.560608	2.389648	0.043454
H	-0.309404	3.141186	-0.512320
H	0.077310	1.542944	-1.306104
H	0.266749	1.570274	1.736337
H	-0.578484	-0.964166	1.610681
C	-3.586614	-0.012362	0.136766
C	-4.185542	-1.207217	0.138363
H	-4.125696	0.831720	0.563890
H	-5.169531	-1.337446	0.573954
H	-3.731362	-2.092014	-0.295020
N	2.189124	-0.408421	-0.090415
C	3.410659	-0.783785	-0.772195
H	4.116321	0.040695	-0.660533
H	3.817810	-1.694745	-0.327401
H	3.234222	-0.967223	-1.836929

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EXO addition of_NMM_to 3_Dend_conf_2_G4MP2
Reaction 1 NMM_[3]Dendralene_DA4
G4MP2
Energy (0K) = -631.211190 au
Enthalpy (298K) = -631.196225 au; Gibbs free energy (298K) = -631.252631 au

C	-1.140932	-0.984641	-0.702937
C	-2.224411	-0.152856	-0.423071
C	-2.027204	1.250181	-0.399149
C	-0.825345	1.847728	-0.674660
C	0.498633	0.767295	1.020335
C	0.227370	-0.594419	0.926700
C	1.822535	1.029317	0.398255
C	1.425881	-1.247324	0.292035
O	1.642323	-2.423848	0.117537
O	2.435966	2.068073	0.305261

H	-0.376712	-0.662302	-1.398186
H	-1.255732	-2.061809	-0.639439
H	-2.806849	1.857829	0.051122
H	-0.678936	2.907003	-0.496588
H	-0.092498	1.391013	-1.326227
H	0.079305	1.466233	1.725526
H	-0.368871	-1.161584	1.626136
C	-3.470992	-0.759395	0.055514
C	-4.653427	-0.156112	0.208741
H	-3.405354	-1.825664	0.265737
H	-5.521331	-0.707699	0.551086
H	-4.810042	0.893535	-0.016633
N	2.277218	-0.210959	-0.086337
C	3.545471	-0.404506	-0.758953
H	4.123424	0.513443	-0.642966
H	4.075812	-1.247177	-0.309678
H	3.405462	-0.611505	-1.824770

##############################

7. Cartesian Coordinates and Energies of TSs for Addition of *N*-Methyl Maleimide (NMM) to [4]Dendralene

Cartesian coordinates and energies of the two lowest energy **ENDO** TSs and the lowest energy **EXO** TS are:

ENDO addition to a terminal diene of [4]Dendralene
Reaction NMM addition_to_[4]Dendralene1
G4MP2
Energy (0K) = -708.486522 au
Enthalpy (298K) = -708.469143 au; Gibbs free energy (298K) = -708.533053 au

C	1.097933	-1.294593	1.481951
C	1.530790	-0.533708	0.409416
C	1.337248	0.890182	0.417116
C	0.700621	1.488012	1.495298
C	-1.355460	0.505975	1.502301
C	-1.185964	-0.869541	1.488118
C	-1.736512	0.940416	0.125194
C	-1.436703	-1.357484	0.101772
O	-1.477801	-2.490772	-0.318389
O	-2.074813	2.031181	-0.272098
H	1.046214	-0.891807	2.483576
H	1.113807	-2.375648	1.411019
H	0.427069	2.535080	1.440915
H	0.774791	1.079733	2.493190
H	-1.622153	1.112805	2.354999
H	-1.276817	-1.542984	2.327123
C	1.648805	1.698519	-0.774562
C	1.909944	3.008151	-0.773064

H	1.691528	1.180061	-1.726936
H	2.111799	3.539402	-1.696262
H	1.942085	3.594265	0.139267
C	2.015857	-1.232691	-0.797573
C	2.755399	-2.342995	-0.782890
H	1.749741	-0.812366	-1.762961
H	3.057452	-2.830457	-1.703079
H	3.092997	-2.797894	0.142672
N	-1.645669	-0.205524	-0.671509
C	-1.957856	-0.227061	-2.085204
H	-2.928930	0.241227	-2.266869
H	-1.202593	0.316445	-2.660476
H	-1.980994	-1.271569	-2.398946

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ENDO addition to the internal diene of [4]Dendralene

Reaction NMM addition_to_[4]Dendralene2
G4MP2
Energy (0K) = -708.488453 au
Enthalpy (298K) = -708.471594 au; Gibbs free energy (298K) = -708.532023 au

C	1.045844	2.466715	0.127133
C	-0.062950	1.914900	-0.472771
C	-1.034213	1.161545	0.229715
C	-0.831486	0.906599	1.582662
C	1.141454	-0.162566	1.644825
C	2.089961	0.608686	0.981057
C	0.795321	-1.316039	0.760071
C	2.360474	-0.018266	-0.343294
O	3.173106	0.284053	-1.185933
O	0.093654	-2.277020	0.991234
H	1.026961	2.789968	1.160337
H	1.830167	2.902779	-0.481160
H	-0.090494	1.877062	-1.557104
H	-1.507945	0.249079	2.116556
H	-0.313861	1.628002	2.199672
H	1.037731	-0.260639	2.715607
H	2.828991	1.250861	1.436658
C	-2.158278	0.516078	-0.499298
C	-2.649163	1.051083	-1.628949
H	-3.452861	0.566382	-2.170325
H	-2.278364	1.984840	-2.036090
C	-2.747250	-0.714562	0.075642
C	-4.055592	-0.963448	0.140798
H	-2.045963	-1.446839	0.469866
H	-4.431896	-1.897879	0.543281
H	-4.793606	-0.242444	-0.197241
N	1.465327	-1.095287	-0.441750
C	1.386587	-1.981512	-1.585232
H	2.189721	-1.705346	-2.269719

H 1.503836 -3.018962 -1.262986
H 0.421966 -1.881407 -2.091677

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EXO addition to terminal diene of [4]Dendralene
Reaction NMM addition_to_[4]Dendralene3
G4MP2
Energy (0K) = -708.484310 au
Enthalpy (298K) = -708.467238 au; Gibbs free energy (298K) = -708.528725 au
C 0.726848 1.078119 -0.718376
C 1.735257 0.123482 -0.745496
C 1.412379 -1.223654 -1.022395
C 0.127518 -1.652063 -1.269522
C -0.910137 -0.995280 0.706582
C -0.568015 0.332342 0.940693
C -2.308725 -1.030114 0.185797
C -1.756590 1.178347 0.595822
O -1.902256 2.371048 0.729235
O -3.002421 -1.982592 -0.086967
H -0.138474 0.980848 -1.361786
H 0.942058 2.089325 -0.393600
H 2.185628 -1.969000 -0.865253
H -0.092953 -2.710252 -1.355882
H -0.609061 -1.001388 -1.721646
H -0.499299 -1.863153 1.197594
H 0.138222 0.685564 1.676278
C 3.113030 0.498338 -0.310695
C 3.728522 1.537969 -0.899322
H 4.727432 1.842830 -0.604159
H 3.256597 2.103874 -1.693789
C 3.808458 -0.235112 0.756282
C 3.294568 -1.143213 1.589915
H 4.853473 0.044666 0.878547
H 3.903426 -1.596244 2.364220
H 2.260169 -1.463291 1.539542
N -2.711384 0.305823 0.061727
C -4.015629 0.718240 -0.414996
H -4.106288 0.576572 -1.496396
H -4.795281 0.130847 0.075965
H -4.133452 1.775982 -0.175603

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8. [3]Dendralene Dimerisation – General Description of Approach and Cartesian Coordinates and Energies

A large number of concerted DA reactions are possible: two dienophilic double bonds, *meta* vs *para* regiochemistries, *endo* and *exo* mode approaches of the dienophilic double bond and 4 possible conformations for the two spectator vinyl groups. To simplify matters, 51 concerted DA TSs were calculated at the B3LYP/6-31G(d) level. IRC analyses of all 51 TSs were carried out in order to identify the bis-pericyclic TSs and also to confirm that the TSs were indeed concerted. In addition, the six lowest energy TSs were then calculated at the G4(MP2) level of theory.

G4(MP2) Energies of **TS 10** and **TS 12** are:

TS 10
Reaction 1 dimerisation_of_[3]Dendralene1
G4MP2
Energy (0K) = -465.959855 au
Enthalpy (298K) = -465.945226 au; Gibbs free energy (298K) = -465.999287 au

C	-2.011114	-0.121111	1.326252
C	-1.365763	1.043115	1.131223
C	-0.713140	1.486696	-0.085017
C	-0.761604	0.706496	-1.235791
H	-2.138247	-0.866450	0.551105
H	-2.442845	-0.356948	2.292421
H	-1.285727	1.726456	1.975213
H	-1.549593	-0.031119	-1.331510
C	0.761604	-0.706496	-1.235791
C	0.713140	-1.486696	-0.085017
C	0.024989	2.744555	-0.028616
C	0.713140	3.348337	-1.009295
H	0.005193	3.233357	0.944377
H	1.226541	4.286148	-0.832403
H	0.787347	2.945565	-2.014085
H	-0.449261	1.143766	-2.177655
H	1.549593	0.031119	-1.331510
H	0.449261	-1.143766	-2.177655
C	1.365763	-1.043115	1.131223
C	2.011114	0.121111	1.326252
H	1.285727	-1.726456	1.975213
H	2.442845	0.356948	2.292421
H	2.138247	0.866450	0.551105
C	-0.024989	-2.744555	-0.028616
C	-0.713140	-3.348337	-1.009295
H	-0.005193	-3.233357	0.944377
H	-1.226541	-4.286148	-0.832403
H	-0.787347	-2.945565	-2.014085

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TS 12

Reaction 1 dimerisation_of_[3]Dendralene2
G4MP2
Energy (0K) = -465.957850 au
Enthalpy (298K) = -465.943507 au; Gibbs free energy (298K) = -465.998064 au

C	0.307548	1.933603	-0.983179
C	-0.674465	1.050379	-1.285260
C	-1.657239	0.556931	-0.368998
C	-1.627840	1.008532	0.957747
H	0.329353	2.496084	-0.059846
H	1.070226	2.185148	-1.710849
H	-0.664866	0.593631	-2.272817
H	-1.308620	2.028596	1.135406
C	-0.052845	0.196166	1.903945
C	1.122979	0.200580	1.154603
C	-2.553421	-0.501859	-0.822191
C	-3.556367	-1.081485	-0.147308
H	-2.368484	-0.841231	-1.840511
H	-4.147958	-1.869789	-0.597976
H	-3.829779	-0.796232	0.863159
H	-2.411887	0.684938	1.634983
H	-0.094675	0.862907	2.760127
H	1.832740	1.001620	1.317839
H	-0.543384	-0.756977	2.075617
C	1.489563	-0.843467	0.223389
C	0.645161	-1.856181	-0.098720
H	0.937342	-2.610034	-0.821538
H	-0.337986	-1.965630	0.337778
C	2.807382	-0.812320	-0.437724
C	3.775526	0.094958	-0.298763
H	2.981820	-1.646057	-1.115485
H	4.707357	0.001424	-0.845391
H	3.692913	0.956587	0.354255

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9. [4]Dendralene Dimerisation – Cartesian Coordinates and Energy of TS 15

TS 15
G4MP2
Energy (0K) = -620.500201 au
Enthalpy (298K) = -620.481621 au; Gibbs free energy (298K) = -620.544831 au

C	-1.005539	1.776699	-0.831118
C	-1.613132	0.578180	-0.720640
C	-1.627876	-0.273956	0.447034
C	-1.005539	0.160492	1.620802
H	-0.484045	2.257126	-0.013041
H	-1.048669	2.331929	-1.761562
H	-2.136679	0.197542	-1.593336
H	-0.913887	1.228557	1.781422
C	1.005539	-0.160492	1.620802
C	1.627876	0.273956	0.447034
C	-2.305571	-1.584324	0.368598
C	-2.737968	-2.252447	1.457292
H	-3.164560	-3.243823	1.364916
H	-2.690450	-1.834738	2.455838
H	-1.166174	-0.404638	2.531731
H	0.913887	-1.228557	1.781422
H	1.166174	0.404638	2.531731
C	1.613132	-0.578180	-0.720640
C	1.005539	-1.776699	-0.831118
H	2.136679	-0.197542	-1.593336
H	1.048669	-2.331929	-1.761562
H	0.484045	-2.257126	-0.013041
C	2.305571	1.584324	0.368598
C	2.737968	2.252447	1.457292
H	3.164560	3.243823	1.364916
H	2.690450	1.834738	2.455838
C	-2.519246	-2.180286	-0.972741
C	-3.638508	-2.785038	-1.371337
H	-1.684045	-2.098755	-1.665047
H	-3.719993	-3.231556	-2.356720
H	-4.513008	-2.847120	-0.731548
C	2.519246	2.180286	-0.972741
C	3.638508	2.785038	-1.371337
H	1.684045	2.098755	-1.665047
H	3.719993	3.231556	-2.356720
H	4.513008	2.847120	-0.731548

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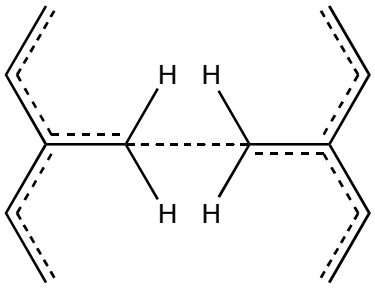
10. Competing Biradical Pathways

Two-step dimerization pathways, proceeding via a biradical intermediate are possible. One such path involves the *anti* mode addition, as shown below:



anti TS for forming biradical intermediate

To date, only a preliminary UB3LYP/6-31G(d) study has been carried out on this dimerisation mode in [3]dendralene. It was found that the bis-pericyclic TS is favoured over the *anti* TS for biradical intermediate formation enthalpically by 1.6 kJ mol^{-1} but the free energy of the *anti* is 3.8 kJ mol^{-1} lower that that of the bis-pericyclic TS. These differences in energy are too small to say which TS is the more stable. Higher level calculations are warranted.

The Cartesian coordinates and energies of the anti-TS are:
ANTI_dimeriz_TS: UB3LYP/6-31G(d)
SCF Energy (no zpe) = -466.7498441 au; Energy+zpe (0K) = -466.5110241 au
Enthalpy (298K) = -466.4961991 au; Gibbs free energy (298K) = -466.5524601 au

C	0.116045	-0.175660	-0.052698
C	0.144873	-0.047445	1.288532
C	1.314245	-0.011084	2.159936
C	2.612013	-0.044402	1.649087
H	1.015032	-0.262215	-0.656642
H	-0.826803	-0.184219	-0.590483
H	-0.813643	0.023392	1.803646
H	2.773214	0.217229	0.607782
C	3.120402	-2.047372	1.441057
C	4.418169	-2.080690	0.930208
C	1.052191	-0.056451	3.594277
C	1.944874	-0.193021	4.594595
H	-0.000180	0.014640	3.870988
H	1.621371	-0.207869	5.630631
H	3.014184	-0.280392	4.423305
H	3.440422	0.210380	2.302997
H	2.291993	-2.302155	0.787147
H	2.959201	-2.309003	2.482362
C	4.680223	-2.035324	-0.504133
C	3.787541	-1.898753	-1.504451

H	5.732595	-2.106414	-0.780844
H	4.111044	-1.883905	-2.540487
H	2.718230	-1.811382	-1.333161
C	5.587542	-2.044329	1.801612
C	5.616370	-1.916114	3.142842
H	6.546058	-2.115166	1.286498
H	6.559218	-1.907556	3.680628
H	4.717383	-1.829559	3.746786

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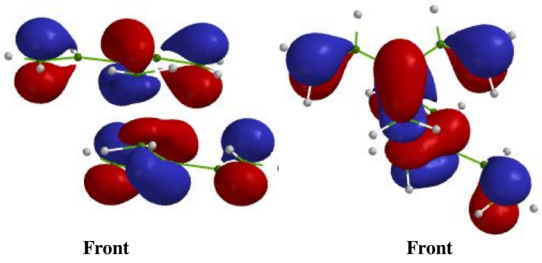
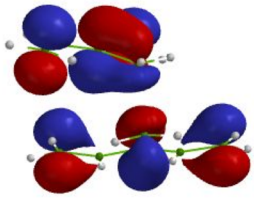
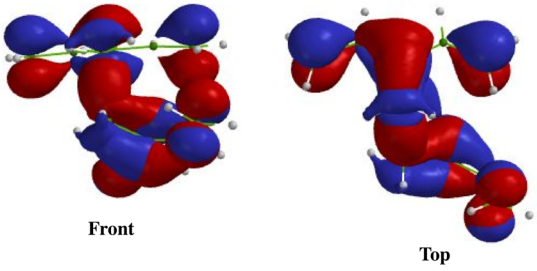
11. B3LYP/6-31G(d) HOMO and LUMO Surfaces for the Various TSs

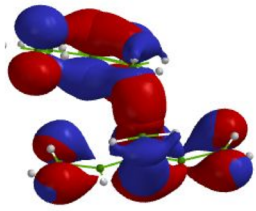
TS 10 HOMO perspectives



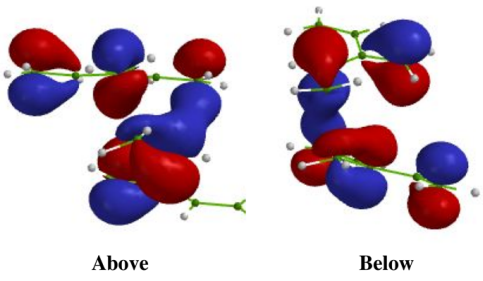


TS 10 LUMO perspectives

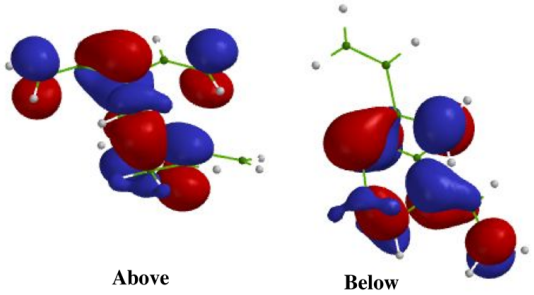




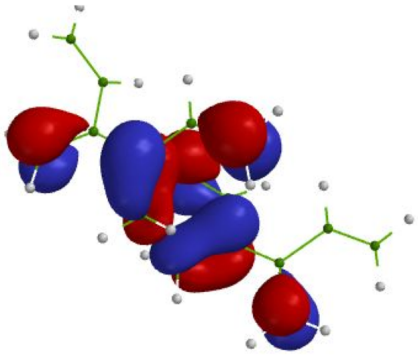
TS 12 HOMO perspectives



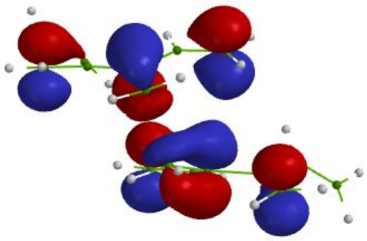
TS 12 LUMO perspectives



TS 15 HOMO perspective

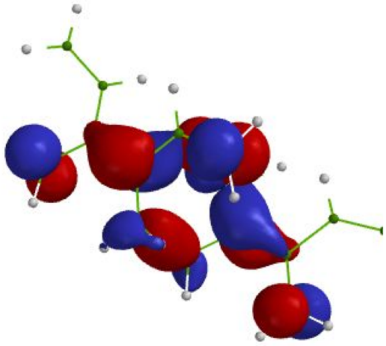


Above



Front

TS 15 LUMO perspective



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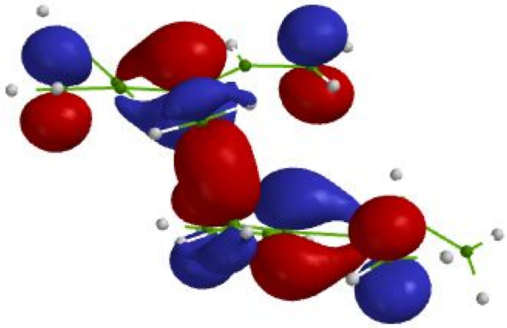

Front