Origin of the Synchronicity on the Transition Structures of Polar Diels-Alder Reactions. Are these reactions [4+2] Processes?

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Table 1S. B3LYP/6-31G* Total energies (in au) for the stationary points corresponding to the cycloaddition reactions of **Cp** with ethylene and the cyano substituted ethylenes, in vacuo and in benzene.

	in vacuo	in benzene
Cp	-194.101064	-194.101777
Et	-78.587457	
1CN	-170.831550	-170.833857
2CN	-263.062684	-263.065537
2cCN	-263.068025	-263.071934
2tCN	-263.069800	-263.073129
3CN	-355.295390	-355.298917
4CN	-447.518276	-447.521168
TS-Et	-272.656774	
TS-1	-364.906426	-364.910743
TS-2	-457.148957	-457.155399
TS-2c	-457.144764	-457.152273
TS-2t	-457.147575	-457.153918
TS-3	-549.380189	-549.388135
TS-4	-641.602696	-641.610687
P-Et	-272.727426	
P-1	-364.967786	-364.971065
P-2	-457.195378	-457.199737
P-2c	-457.200062	-457.206358
P-2t	-457.203368	-457.208494
P-3	-549.423888	-549.430100
P-4	-641.640704	-641.647126

Table 2S. B3LYP/6-31G* Sum of electronic and thermal enthalpies (H) and free energies (G) (in au), entropies (S) (in cal·mol⁻¹·K⁻¹), and relative enthalpies (ΔH), entropies (ΔS) and free energies (ΔG) (in kcal·mol⁻¹), computed at 20°C and 1 atm., for the stationary points corresponding to the cycloaddition reactions of **Cp** with ethylene and the cyano substituted ethylenes.

	H	ΔH	S	ΔS	G	ΔG
Cp	-194.006801		66.8		-194.037999	
Et	-78.534339		53.6		-78.559388	
1CN	-170.777559		65.2		-170.808031	
2CN	-263.008360		75.2		-263.043511	
2cCN	-263.013447		75.4		-263.048691	
2tCN	-263.015244		75.4		-263.050458	
3CN	-355.240644		85.4		-355.280520	
4CN	-447.463429		95.2		-447.507908	
TS-Et	-272.507656	21.0	77.3	-43.1	-272.543748	33.7
TS-1	-364.756455	17.5	87.2	-44.8	-364.797183	30.7
TS-2	-456.998417	10.5	97.3	-44.7	-457.043876	23.6
TS-2c	-456.994235	16.3	96.2	-46.0	-457.039173	29.8
TS-2t	-456.997029	15.7	96.1	-46.1	-457.041898	29.2
TS-3	-549.229425	11.3	106.0	-46.2	-549.278936	24.8
TS-4	-641.451983	11.5	114.5	-47.5	-641.505448	25.4
P-Et	-272.573743	-20.5	73.2	-47.2	-272.607946	-6.6
P-1	-364.813640	-18.4	82.7	-49.4	-364.852250	-3.9
P-2	-457.041411	-16.5	91.8	-50.2	-457.084315	-1.8
P-2c	-457.045809	-16.0	92.2	-50.0	-457.088877	-1.4
P-2t	-457.049013	-16.9	92.3	-49.8	-457.092152	-2.3
P-3	-549.269929	-14.1	101.4	-50.8	-549.317277	0.8
P-4	-641.487265	-10.7	110.3	-51.7	-641.538805	4.5

The B3LYP/6-31G* computed total energies, unique frequency imaginaries and Cartesian coordinates of the transition structures corresponding to the cycloadditions between cyclopentadiene and the cyanide substituted ethylenes **TS-1**, **TS-2**, **TS-2c**, **TS-2t**, **TS-3** and **TS-4**.

TS-1

E(B3LYP/6-31G*) = -364.906426154 au.

1 imaginary frequencies -457.6676 cm⁻¹

C	0.000000000000	0.000000000000	0.000000000000
C	0.000000000000	0.000000000000	1.389502000000
C	1.329738606481	0.000000000000	1.846854142697
C	2.195854539109	-0.074612864570	0.740880117926
C	2.113724283686	-2.084437124659	0.238879122277
C	1.382089278248	0.373563595703	-0.459332906415
C	0.822726854377	-2.319686745883	-0.254843452935
C	-0.161337792141	-2.984213102793	0.528937482580
H	-0.882465528069	0.041258211519	-0.628337756768
H	-0.878189493792	-0.099614031836	2.017278540804
H	1.633184954819	-0.081499964257	2.885361324721
H	3.264260380420	0.108893476371	0.814427695477
H	2.925469426733	-2.017690392410	-0.480035279689
H	2.395862560797	-2.518678272103	1.191727557578
H	1.690625324047	-0.028458383339	-1.426732868461
H	1.444906702688	1.473254280795	-0.520794306587
H	0.625334492465	-2.272993682231	-1.320855622844
N	-0.963347303531	-3.532916296742	1.174688340058

TS-2

E(B3LYP/6-31G*) = -457.148956950 au.

1 imaginary frequencies -373.3635 cm⁻¹

C	0.000000000000	0.000000000000	0.000000000000
C	0.000000000000	0.000000000000	1.379214530000
C	1.336722973942	0.000000000000	1.836091133495
C	2.208804350075	-0.133267487574	0.735397029634
C	2.299376602691	-2.099164026205	0.460875925322
C	1.391881359764	0.242176850307	-0.492146098864
C	1.057320990989	-2.590913692938	-0.009011178462
C	0.109979154931	-3.129736745333	0.908951812592
C	0.805737130859	-2.727369906578	-1.404672658845
H	-0.873843062467	-0.033609173489	-0.640099784628
H	-0.877066162939	-0.063562755603	2.012475534603
H	1.638668836831	-0.031119942626	2.877865533162

H	3.265096566195	0.112172899944	0.810643966663
H	3.110726718348	-2.068556166842	-0.261477381073
H	2.608890266593	-2.411972958172	1.452360571068
H	1.646809114892	-0.263479775866	-1.425604158423
H	1.522250549056	1.324049282129	-0.664114935018
N	-0.635281103839	-3.561984620785	1.695054863035
N	0.635025800609	-2.820972739873	-2.555129774655

TS-2c

E(B3LYP/6-31G*) = -457.144763796 au.

1 imaginary frequencies -461.0871 cm⁻¹

C	0.000000000000	0.000000000000	0.000000000000
C	0.000000000000	0.000000000000	1.402564930000
C	1.325107630955	0.000000000000	1.857030386290
C	2.185941538494	-0.000642548727	0.749679632772
C	1.938693466466	-2.116493148056	0.089028447940
C	1.372141086488	0.451478538415	-0.438858023317
H	2.719836477162	-2.015999134172	-0.658240616665
C	2.337586819254	-2.828048299083	1.264563032520
C	0.600257729578	-2.116535716460	-0.370096593502
C	-0.436315713806	-2.827821949126	0.313148556612
H	0.442196121305	-2.015778919128	-1.439478938374
H	-0.890200953869	0.108340164837	-0.610614037021
H	-0.877503377113	-0.121937613344	2.027088389633
H	1.634564236992	-0.122044977205	2.888659855405
H	3.263544169893	0.107479145854	0.813987631706
H	1.707222898129	0.097495157023	-1.416300048585
H	1.381472123692	1.553472715398	-0.465058043189
N	-1.302661508449	-3.390527039240	0.849656102335
N	2.692176592581	-3.390999488089	2.219745590884

TS-2t

E(B3LYP/6-31G*) = -457.147575029 au.

1 imaginary frequencies -447.4737 cm⁻¹

C	0.000000000000	0.000000000000	0.000000000000
C	0.000000000000	0.000000000000	1.404763740000
C	1.325534046886	0.000000000000	1.857766535879
C	2.185353377833	0.010045782215	0.750808664117
C	1.925146474917	-2.129517225293	0.087684962745
C	1.369360637808	0.455966462148	-0.437483421456
C	2.987182916286	-2.141233551249	-0.868300641152
H	2.156149074807	-2.592031696174	1.040676336928
C	0.581089704304	-2.114238562507	-0.356636722826
C	-0.419525066831	-2.802769036450	0.400102677977

H	0.390974738061	-2.062701417600	-1.424565116149
H	-0.891671136065	0.112978063707	-0.607747001133
H	-0.877363233459	-0.123835514432	2.029205133200
H	1.634673003418	-0.111535195473	2.891530457100
H	3.263716270634	0.112485477598	0.803516095761
H	1.714681572902	0.107043332978	-1.412272864215
H	1.372301597286	1.558153206336	-0.459260875787
N	-1.237156833051	-3.354528746231	1.018780518094
N	3.855090344157	-2.125886359760	-1.645539560369

TS-3

E(B3LYP/6-31G*) = -549.380189114 au.

1 imaginary frequencies -385.7521 cm⁻¹

C	0.000000000000	0.000000000000	0.000000000000
C	0.000000000000	0.000000000000	1.418036550000
C	1.325642222890	0.000000000000	1.878640358012
C	2.179066059548	0.103619693391	0.788013304415
C	1.610431907077	-2.302256519380	-0.055287635235
C	1.377108661720	0.487713372324	-0.416613153708
C	2.652613321011	-2.285296585394	-1.028521984618
C	1.856402307003	-2.988075856410	1.170993731325
C	0.283030225162	-1.930927716414	-0.449663502974
C	-0.846845773180	-2.576711748487	0.172923687669
H	0.150392470347	-1.808275815345	-1.522824853477
H	-0.892587450500	0.235680230759	-0.573164961885
H	-0.879582501278	-0.134820537572	2.037318529545
H	1.632045634491	-0.149073767701	2.907220042479
H	3.262256010325	0.106462418412	0.824889353808
H	1.760871548932	0.123903449123	-1.371513734027
H	1.339890281345	1.587878303026	-0.478454226753
N	-1.783293400910	-3.063441212048	0.659313923064
N	3.485392498899	-2.243163103640	-1.843627365714
N	2.048886385306	-3.538658805266	2.179525651244

TS-4

E(B3LYP/6-31G*) = -641.602695927 au.

1 imaginary frequencies -413.5221 cm⁻¹

C	0.000000000000	0.000000000000	0.000000000000
C	0.000000000000	0.000000000000	1.413303680000
C	1.318399922730	0.000000000000	1.861280371063
C	2.179477170408	-0.003044019363	0.740278441370
C	1.944888357835	-2.101584219919	0.117158920627
C	1.365963737687	0.458327236188	-0.441641561670
C	3.004748904158	-2.120195366554	-0.856737274109

C	2.255324387439	-2.783134500950	1.347089803062
C	0.565791940041	-2.102392302618	-0.352093756817
C	-0.430274749984	-2.782880453392	0.433946160827
C	0.319137715844	-2.119790025693	-1.769988127576
H	-0.890828607893	0.094813612363	-0.611448212392
H	-0.878396094851	-0.114724257575	2.037491949808
H	1.634553558477	-0.115130012478	2.891409354854
H	3.258427597527	0.091686969910	0.798411388629
H	1.698852449947	0.118475938625	-1.423647976319
H	1.372616224093	1.559924903478	-0.456220532654
N	-1.252733973784	-3.305418103761	1.068057000747
N	0.097677286133	-2.094091115238	-2.911462206586
N	3.876106769719	-2.095371197384	-1.626619704994
N	2.520809428699	-3.306365627376	2.350715040620