

Supplementary Material

Unveiling the Different Reactivity of Bent and Linear Three-Atom-Components Participating in [3+2] Cycloaddition Reactions

Mar Ríos-Gutiérrez,^{*a} Luis R. Domingo,^a Fatemeh Ghodsi^b

^a Department of Organic Chemistry, University of Valencia, Dr Moliner 50, 46100 Burjassot, Valencia, Spain

^b Department of Chemistry, University of Sistan and Baluchestan, Zahedan, Iran

email: rios@utopia.uv.es

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Table S1. MPWB1K/6-311G(d,p) gas-phase total electronic energies, in a.u., of the stationary points involved in the 32CA reactions of TACs **1-8** with ethylene **9**.

	TAC	MC-n	TS-n	CA-n
ethylene	-78.552848			
1	-133.837059	-212.392758	-212.389771	-212.513907
2	-149.876570	-228.433098	-228.419234	-228.524020
3	-165.916866	-244.474252	-244.444998	-244.538593
4	-169.750050	-248.308204	-248.284052	-248.368246
5	-132.620870	-211.175604	-211.162310	-211.303513
6'	-148.694350	-227.248800	-227.221300	-227.315090
6''	-148.651349	-227.205475	-227.191473	-227.313995
7	-164.740775	-243.298496	-243.259959	-243.341410
8	-168.532259	-247.087461	-247.060254	-247.166050

Table S2. MPWB1K/6-311G(d,p) gas-phase total electronic energies, in a.u., of the stationary points involved in the 32CA reactions of TACs **1-8** with DCE **10**.

	TAC	MCo-n	TSo-n	CAo-n
DCE	-262.988892			
1	-133.837059			-396.947875
2	-149.876570	-412.878639	-412.877304	-412.944505
3	-165.916866	-428.912199	-428.896290	-428.964587
4	-169.750050	-432.751300	-432.739455	-432.797076
5	-132.620870	-395.620740	-395.619747	-395.731022
6'	-148.694350	-411.689624	-411.665255	-411.737771
6''	-148.651349	-411.648530	-411.638635	-411.737356
7	-164.740775	-427.733598	-427.694784	-427.759921
8	-168.532259	-431.527581	-431.496811	-431.582214
		MCm-n	TSm-n	CAm-n
2		-412.874814	-412.872861	-412.950873
4		-432.753337	-432.730784	-432.789673
5		-395.616378	-395.612628	-395.727411
6'		-411.687397	-411.675887	-411.732903
6''		-411.647858	-411.639973	-411.7376652
7		-427.738564	-427.703604	-427.759330
8		-431.523606	-431.499454	-431.582168

TS-1

E(RmPW+HF-B95) = -212.389771019 a.u.

Imaginary frequency = -276.6879 cm⁻¹

C	-1.5157084150	0.6734427878	-0.0596239800
C	-1.5157054004	-0.6734479439	-0.0596271926
C	0.8927783252	-1.1869508102	0.1988182474
C	0.8927737083	1.1869545989	0.1988224951
H	1.2175078670	2.0531642193	-0.3453986993
H	0.7026195580	1.2644204002	1.2516001372
H	-1.7260290532	1.2334889627	0.8363566085
H	-1.5275811196	-1.2350935219	-0.9784206923
H	1.2175158322	-2.0531572219	-0.3454059825
H	0.7026244840	-1.2644210539	1.2515955843
H	1.5545108693	0.0000057477	-1.2336511532
N	1.2422675767	0.0000033985	-0.2793122757
H	-1.7260236311	-1.2334993503	0.8363506639
H	-1.5275866016	1.2350927867	-0.9784147608

TS-2

E(RmPW+HF-B95) = -228.419234362 a.u.

Imaginary frequency = -448.7598 cm⁻¹

C	-1.4227118010	-0.6303625004	-0.0609686667
C	-1.3574521165	0.7300700663	-0.0702646962
C	0.8522760778	1.0908875455	0.2094266683
N	0.7633806473	-1.2348663236	0.1349237921
H	1.5135127539	-0.1051914534	-1.2347573436
H	0.5548403255	-1.1255796541	1.1183424385
H	-1.4760458824	-1.1955905616	-0.9738950074
H	-1.6301704506	1.2966366133	0.8053950244
H	0.7094801733	1.1555142870	1.2728514991
H	1.2220853510	1.9615053695	-0.3048662846
N	1.2107954653	-0.0874008043	-0.2759642301
H	-1.7098342611	-1.1633270658	0.8307142929
H	-1.4002062824	1.2732494817	-1.0000194868

TS-3

E(RmPW+HF-B95) = -244.444996876 a.u.

Imaginary frequency = -572.2743 cm⁻¹

C	1.2995902239	0.6876369168	-0.0638179214
C	1.2995918446	-0.6876338771	-0.0638181637
N	-0.7595400005	-1.1476698590	0.1425827583
N	-0.7595423169	1.1476681649	0.1425836129
H	-1.4351157889	-0.0000010398	-1.2495499195
H	-0.6141462532	1.0626621005	1.1399158953
H	1.3825349747	1.2348553910	-0.9861879471
H	1.6140742734	-1.2291905855	0.8139622355
H	-0.6141441016	-1.0626642663	1.1399151216
N	-1.1864452466	-0.0000011053	-0.2740829175
H	1.6140715340	1.2291940505	0.8139626018
H	1.3825378571	-1.2348518906	-0.9861883562

TS-4

E(RmPW+HF-B95) = -248.284052056 a.u.

Imaginary frequency = -509.7225 cm⁻¹

C	-1.3493195181	-0.6447922733	0.0068598994
C	-1.3125839954	0.7169268104	0.1214316113
C	0.7970115261	1.0636952112	-0.2325939215
O	0.6880351649	-1.1555601650	-0.2060072589
H	-1.4058945666	-1.2762440749	0.8756804489
H	-1.3809626296	1.1786349940	1.0935934156
H	1.1393298245	1.9531830367	0.2701980542
N	1.2027720557	-0.0906264583	0.2478707136
H	-1.6288349092	1.3342837803	-0.7036787178
H	-1.5885383989	-1.1160886010	-0.9297048349
H	0.6176105580	1.1004098114	-1.2902047932
H	1.5062378886	-0.1101500715	1.2136953833

TS-5

E(RmPW+HF-B95) = -211.162310439 a.u.

Imaginary frequency = -424.2173 cm⁻¹

C	1.4086021089	-0.6785978221	-0.0000946179
C	1.4566562542	0.6707431014	-0.0000475339
C	-0.8540750477	1.2409951672	0.0000872169
C	-0.9760356176	-1.1530468630	0.0000058235
H	1.5146481181	-1.2364949477	0.9154469778
H	1.5969352111	1.2249968177	-0.9127541940
H	-1.4894530331	2.1184236183	0.0001507653
H	-1.0780566751	-1.6925086594	-0.9268213432
H	-1.0779649103	-1.6925763251	0.9268036945
H	1.5145574988	-1.2364277775	-0.9156876310
N	-1.2615592859	0.1067528014	0.0000659364
H	1.5970253788	1.2249298888	0.9126859055

TS-6'

E(RmPW+HF-B95) = -227.221300270 a.u.

Imaginary frequency = -535.1528 cm⁻¹

C	1.4158728996	-0.5810951482	0.0000033688
C	1.2253346372	0.7691121659	-0.0001029937
C	-0.9428975096	1.0444585446	-0.0000571780
N	-0.7450092139	-1.2981132739	0.0001322746
H	-1.2347273798	1.5402898783	0.9134859374
H	-1.2347853448	1.5401368191	-0.9136648368
H	1.3580568467	1.3321538692	-0.9097870860
H	1.6135270950	-1.1152766804	0.9136933783
N	-1.2093995534	-0.2614147296	0.0000605338
H	1.3581146523	1.3323053430	0.9094788966
H	1.6134688709	-1.1154287880	-0.9136102951

TS-6''

E(RmPW+HF-B95) = -227.191472518 a.u.

Imaginary frequency = -433.3003 cm⁻¹

N	0.00000000	0.00000000	1.19481275
N	0.73132286	0.00000000	2.20194385
H	0.42448022	-0.71663097	2.85043239
H	-0.68501289	0.38650336	-0.72819693
C	2.22775030	-0.33057099	-0.31394334
C	2.69135964	-0.39807816	0.95367924
H	2.84848251	-1.34731611	1.43796652
H	3.08824321	0.46679300	1.45340020
H	2.04791575	-1.22482239	-0.88631995
H	2.30386349	0.58752087	-0.87535581

TS-7

E(RmPW+HF-B95) = -243.259959411 a.u.

Imaginary frequency = -557.7752 cm⁻¹

C	-1.3133272946	-0.6091869634	0.0046274970
C	-1.2116188642	0.7565829151	0.0143958820
N	0.8639061681	1.0083155250	-0.1039535987
N	0.7037120271	-1.2245791313	0.0012570077
H	-1.5303092254	-1.1278789539	-0.9137582278
H	-1.3313836316	1.3038080457	0.9347546458
H	1.4427655068	1.6311477771	0.4422185094
N	1.2053152294	-0.1916010411	0.0186848085
H	-1.3549031663	1.3229019383	-0.8884594351
H	-1.5190037494	-1.1475141114	0.9132229114

TS-8

E(RmPW+HF-B95) = -247.060253902 a.u.

Imaginary frequency = -516.4676 cm⁻¹

C	-1.3277972094	-0.7061594774	0.0000042818
C	-1.3383708922	0.6488802156	0.0000250687
C	0.7651088125	1.1438682205	0.0000086140
O	0.9395714186	-1.1128626377	-0.0000277750
H	-1.3927342171	-1.2674295166	0.9153588627
H	-1.5207004908	1.1878143142	0.9162690447
H	1.0763422941	2.1636119001	0.0000205930
N	1.2342566550	0.0509273154	-0.0000134092
H	-1.5207213291	1.1878422482	-0.9161983298
H	-1.3927550414	-1.2674015823	-0.9153659510

TSo-2

E(RmPW+HF-B95) = -412.877304061 a.u.

Imaginary frequency = -234.7809 cm⁻¹

C	-0.1264971299	-0.1902310597	1.5422889487
C	0.7661981895	0.0269784202	0.5244628870
C	-1.1703990087	-0.0587738830	-1.4644413571
N	-2.0104591496	-0.5281184513	0.6764241429
H	-2.2873197251	1.1043136195	-0.3359049729
H	-1.7328354097	-1.4717927227	0.4336089442
H	-0.4742195874	0.6424423466	2.1254241878
H	-0.7377886107	-1.0346628747	-1.5937352436

H	-1.1268137404	0.6858684864	-2.2367878905
N	-1.8934656272	0.1788848708	-0.4188225000
H	-0.1588454052	-1.1529019375	2.0212060645
C	1.4211511392	-1.0607092537	-0.1037428344
C	1.0593012393	1.3476419706	0.0981893070
N	1.8996045564	-1.9698538682	-0.6127266807
N	1.2608682695	2.4312983368	-0.2168000028

TSo-3

E(RmPW+HF-B95) = -428.896289962 a.u.

Imaginary frequency = -385.7188 cm⁻¹

C	0.3016224203	-0.0072272616	1.4375281961
C	-0.6963315132	0.0716518351	0.4567343025
N	1.0813200330	-0.2339527793	-1.4597003967
N	1.9464217386	0.1226498308	0.6430783875
H	2.0706972163	-1.5080412633	-0.4349323420
H	1.8678953753	1.1065574808	0.4132747370
H	0.4030651162	-0.9475847018	1.9528839395
H	0.8376433282	0.7519987770	-1.4002760623
N	1.7966919874	-0.5357887530	-0.4790255560
H	0.4496844651	0.8527033997	2.0711662769
C	-1.0585808063	1.3399893172	-0.0446212997
C	-1.3948771519	-1.0861985307	0.0466683706
N	-1.2395680058	2.3931243201	-0.4645772680
N	-1.9424562033	-2.0521796709	-0.2385352854

TSo-4

E(RmPW+HF-B95) = -432.739455298 a.u.

Imaginary frequency = -351.4132 cm⁻¹

C	-0.9506543409	-0.4231626814	-1.4059013847
N	-1.8511276307	-0.1152040252	-0.5392429396
O	-1.8362623566	-0.6576132977	0.6303291194
H	-2.3562809840	0.7569270551	-0.6252588174
H	-0.4502599689	-1.3697346118	-1.3200366377
H	-0.8701138704	0.1797009842	-2.2934256574
C	0.6398956459	0.1145033918	0.4484663836
C	-0.3291896042	-0.2402980266	1.4030513223
H	-0.7108792142	0.5538631220	2.0226614791
H	-0.1935028505	-1.1786681354	1.9121622881
C	0.7842000353	1.4734033076	0.0840428361
N	0.8244704172	2.5827443705	-0.2061419584
C	1.5853640124	-0.8340850355	0.0002020245
N	2.3014087094	-1.6450274175	-0.3813170576

TSo-5

E(RmPW+HF-B95) = -395.619746485 a.u.

Imaginary frequency = -217.4932 cm⁻¹

C	0.7411439296	0.0000036235	0.5700079344
C	-0.1108163585	0.0000105610	1.6293915364
C	-2.2086060475	0.0000010278	0.6894433501

C	-1.2210520943	-0.0000145926	-1.5386234422
H	-0.3265413783	0.9189045066	2.1436964911
H	-3.2351127591	0.0000023746	1.0345748019
H	-0.9784124113	0.9397522711	-2.0062021208
H	-0.9784102062	-0.9397880183	-2.0061877960
N	-1.9133627123	-0.0000074380	-0.4810385097
H	-0.3265391606	-0.9188761779	2.1437102994
C	1.1985478631	1.2194495809	0.0046840756
C	1.1985507752	-1.2194497346	0.0047023957
N	1.5450606360	2.2173477344	-0.4387161641
N	1.5450659243	-2.2173537244	-0.4386828520

TSo-6'

E(RmPW+HF-B95) = -411.665254571 a.u.

Imaginary frequency = -505.5970 cm⁻¹

C	0.4361715143	0.0000007179	1.4472430483
C	-0.4981291044	-0.0000001156	0.4187325915
C	0.9027833811	-0.0000021834	-1.4025617218
N	2.2091649841	-0.0000003311	0.5389729865
H	0.7290092743	-0.9290639826	-1.9226643440
H	0.7290179259	0.9290691546	-1.9226512217
H	0.6094502418	-0.9139277829	1.9882392690
N	1.9156461541	-0.0000030452	-0.5671865899
H	0.6094504599	0.9139302292	1.9882375010
C	-1.1447239726	1.2174792183	0.0538430090
C	-1.1447242329	-1.2174799084	0.0538450162
N	-1.6297755176	2.2111026341	-0.2411250315
N	-1.6297761080	-2.2111036117	-0.2411215126

TSo-6''

E(RmPW+HF-B95) = -411.638635090 a.u.

Imaginary frequency = -405.1736 cm⁻¹

H	0.31549970	-0.72046031	2.86120116
H	-0.48335228	0.28353260	-0.90722455
C	2.45085288	-0.49782287	0.17608967
C	2.52960136	-0.40885432	1.54816364
H	2.62985368	-1.31797402	2.11502398
H	2.93074957	0.48512523	1.98816050
C	2.29720669	-1.76283056	-0.45388993
N	2.16864247	-2.79378933	-0.93562703
C	2.74219697	0.62628308	-0.64408486
N	2.96676498	1.54276765	-1.29331391

TSo-7

E(RmPW+HF-B95) = -427.694783876 a.u.

Imaginary frequency = -558.6975 cm⁻¹

C	0.4898361448	-0.1202234474	1.3846722498
C	-0.4717916790	-0.0000834431	0.3819487360
H	0.5816970684	-1.0725846804	1.8780713796
H	0.8327913214	0.6652007052	-2.0001781431

N	2.1734875180	-0.1907781195	0.4966548106
N	1.8836193205	-0.0637023043	-0.6130845369
N	0.8596104544	-0.0815910488	-1.3147643692
H	0.7130682561	0.7473174451	1.9799410425
C	-1.2405177132	-1.1387543140	-0.0044047829
C	-1.0267715484	1.2830311186	0.0939646696
N	-1.4414114594	2.3238428054	-0.1356170684
N	-1.8557156835	-2.0604217170	-0.2836109876

TSo-8

E(RmPW+HF-B95) = -431.496811089 a.u.

Imaginary frequency = -561.0326 cm⁻¹

C	0.4685356873	0.0000668706	-1.4002831528
C	-0.4970110627	0.0000083188	-0.4080028061
C	0.8711973515	-0.0000910982	1.3871521280
O	2.1908781767	0.0000141359	-0.4446022701
H	0.6932924443	-0.9181628061	-1.9112276070
H	0.4575992604	-0.0001471885	2.3702237434
N	1.8427760588	-0.0000521359	0.7194911049
H	0.6932896055	0.9183559491	-1.9111220972
C	-1.1564933309	-1.2171000780	-0.0576153033
C	-1.1564974736	1.2170743288	-0.0574757335
N	-1.6698190360	-2.1982662530	0.2285686392
N	-1.6698266814	2.1982059566	0.2288203545

TSm-2

E(RmPW+HF-B95) = -412.872860925 a.u.

Imaginary frequency = -246.7207 cm⁻¹

C	-0.7367567592	0.0337664451	0.5107786950
C	0.1500494335	-0.1086573557	1.5387106882
C	2.1588245343	-0.4295841401	0.5245205253
N	0.9623557674	-0.0922767190	-1.4587955764
H	2.1669514908	1.1634074786	-0.6782417102
H	0.7025661429	-1.0634003654	-1.3152232079
H	0.2318261130	-1.0557705984	2.0415108482
H	2.0079762588	-1.4938598623	0.5296947726
H	2.9457249747	-0.0036699691	1.1195192932
N	1.8403707180	0.2113382564	-0.5908347217
H	0.4781812281	0.7627742483	2.0763159837
C	-1.3955821348	-1.1000695017	-0.0309709675
C	-1.0927118246	1.3300385787	0.0520499127
N	-1.8757942025	-2.0496050873	-0.4552070078
N	-1.3499177406	2.4012185919	-0.2594215274

TSm-4

E(RmPW+HF-B95) = -432.730784123 a.u.

Imaginary frequency = -430.9572 cm⁻¹

C	2.0098108567	-0.7022937491	0.4113299157
N	1.7934347489	0.0696287434	-0.6411640092
O	0.7843716290	-0.1131258513	-1.3387872523

H	2.2154249885	0.9939996474	-0.6693306381
H	1.7378254473	-1.7341473055	0.2806017096
H	2.8667280694	-0.4617818657	1.0179442897
C	0.2932809627	-0.2657907734	1.4344219392
C	-0.6342602874	0.0409771974	0.4560323797
H	0.2148372837	-1.2222798172	1.9227056484
H	0.6708776246	0.5415469652	2.0384437889
C	-0.8714641082	1.4034849333	0.1364031184
N	-1.0033733564	2.5224689570	-0.0675350917
C	-1.5004954989	-0.9546280817	-0.0623265014
N	-2.1854693599	-1.7852249998	-0.4492832969

TSm-5

E(RmPW+HF-B95) = -395.612629670 a.u.

Imaginary frequency = -297.3054 cm⁻¹

C	0.6576662225	0.0000000736	-0.5073538195
C	-0.2587317071	0.0000001933	-1.5124671973
C	-2.3727704889	-0.0000000121	-0.4695998527
C	-0.9536365639	-0.0000002930	1.4912397042
H	-0.4991497128	-0.9212060053	-2.0113890018
H	-2.7849124465	-0.9290977855	-0.8246825724
N	-1.8459606588	-0.0000001680	0.7138483996
H	-0.4991497861	0.9212065162	-2.0113887362
C	1.2150076784	-1.2200477634	-0.0301008488
C	1.2150075669	1.2200478307	-0.0301004725
N	1.6533110037	-2.2160301334	0.3253900802
N	1.6533108005	2.2160301302	0.3253907677
H	-2.7849124229	0.9290978658	-0.8246823257
H	-0.8905964851	-0.0000004447	2.5643778753

TSm-6'

E(RmPW+HF-B95) = -411.675886508 a.u.

Imaginary frequency = -404.5719 cm⁻¹

C	0.6573460571	-0.0000372566	0.4807619518
C	-0.3534311506	-0.0000562860	1.4241038035
C	-2.2069264916	0.0000088508	0.5155382840
N	-1.0175990862	0.0000687182	-1.5582475072
H	-2.7112994454	-0.9160982260	0.7805067681
H	-2.7112695900	0.9161119259	0.7805773324
H	-0.5313798453	0.9123395425	1.9675429946
N	-1.7819442418	0.0000502703	-0.7494700590
H	-0.5314100849	-0.9124872278	1.9674741730
C	1.2156250048	1.2221900049	0.0335942057
C	1.2155817539	-1.2222493933	0.0334987441
N	1.6354710392	2.2339275962	-0.3033076463
N	1.6353920808	-2.2339755191	-0.3034820448

TSm-6''

E(RmPW+HF-B95) = -411.639973398 a.u.

Imaginary frequency = -375.0976 cm⁻¹

C	-2.1896582230	-0.2797059224	0.5568207906
N	-1.8746987275	-0.0760390346	-0.5754993017
N	-1.0366163862	0.0092586806	-1.4609817834
H	-1.0023772862	0.9560480030	-1.8322192508
H	-3.1157937295	-0.5749895767	1.0088077753
C	0.6383083873	-0.0121272388	0.5109027406
C	-0.2778122264	-0.1930788267	1.5126488167
H	-0.3811225290	-1.1718803513	1.9498244566
H	-0.5631320053	0.6488818477	2.1183992821
C	1.3132071808	-1.1188906299	-0.0685746129
N	1.8585536424	-2.0288814530	-0.4975918812
C	1.0240166922	1.2992193381	0.1247147756
N	1.2964042105	2.3711241639	-0.1735768075

TSm-7

E(RmPW+HF-B95) = -427.703603603 a.u.

Imaginary frequency = -524.0206 cm⁻¹

C	0.5625459710	0.0247472110	0.4069185096
C	-0.4407623002	-0.0879151160	1.3709995252
N	-2.0624109093	-0.2530371967	0.4872864494
N	-0.9548878827	-0.0683876894	-1.4814311740
H	-0.6748748991	0.7972156942	1.9396282266
H	-2.8510258087	0.3013225540	0.7890958458
N	-1.7960261624	-0.0988215997	-0.7322565484
H	-0.5079430341	-1.0176894619	1.9083865300
C	1.3030858016	-1.1203634724	0.0162766094
C	1.0422110049	1.3090564543	0.0432522407
N	1.8824088462	-2.0625979560	-0.2792244502
N	1.3946213729	2.3646215786	-0.2268177640

TSm-8

E(RmPW+HF-B95) = -431.499453503 a.u.

Imaginary frequency = -508.4754 cm⁻¹

C	-0.5814627112	0.0000016012	0.4711434927
C	0.3940441618	-0.0000007856	1.4403158282
C	2.1843981506	-0.0000050620	0.4858062361
O	0.9450895526	-0.0000019367	-1.4173055290
H	0.5833427376	-0.9200106342	1.9681426711
H	3.0890628265	-0.0000074222	1.0523277165
N	1.8493456718	-0.0000042270	-0.6564579168
H	0.5833471688	0.9200081107	1.9681427403
C	-1.1651745383	1.2203096183	0.0370908422
C	-1.1651804125	-1.2203035723	0.0370907447
N	-1.6270934573	2.2189658220	-0.2755493223
N	-1.6271041503	-2.2189575208	-0.2755495038

