

SUPPORTING INFORMATION/3

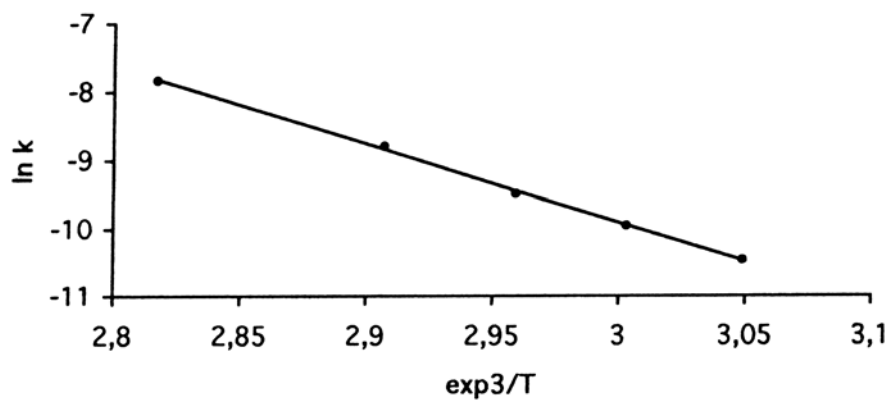
Kinetic Control in the Palladium-Catalyzed Synthesis of C₂-Symmetric Hexabenzotriphenylene. A Conformational Study.

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Arrhenius plot

$$\ln k = \ln A - E_a/RT$$

$$E_a = 22.8 \text{ kcal/mol}$$

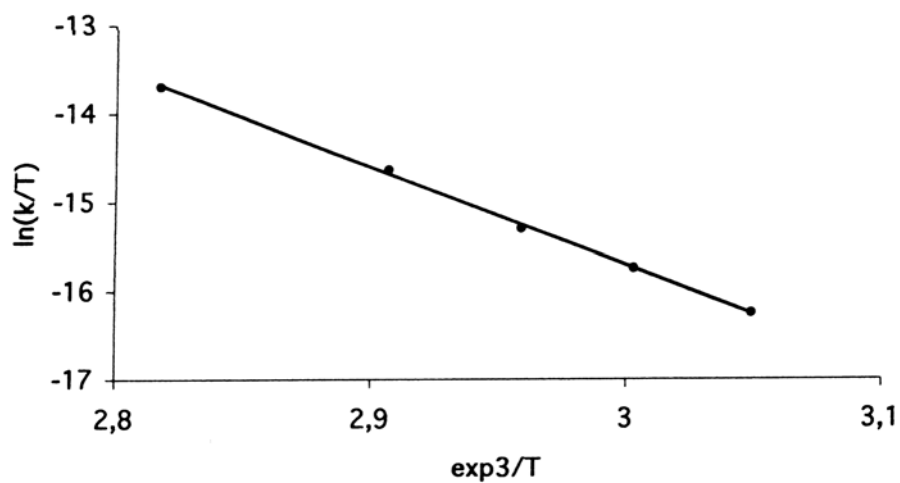


Eyring plot

$$\ln(k/T) = \ln(kb/h) - \Delta H^\ddagger / RT + \Delta S^\ddagger / R$$

$$\Delta H^\ddagger = 22.0 \text{ kcal/mol}$$

$$\Delta S^\ddagger = -12.3 \text{ cal/mol}$$



Calculated total energies (au) for the conformation C2 and the transition states C2-C2 and C2-D3

	C2	C2C2 (TS-I)	C2D3 (TS-II)
AM1*	214,788567	226,020494	237,902446
RHF/3-21G	-1595,526451	-1595,503774	-1595,476778
RHF/6-31G	-1603,937097	-1603,916682	-1603,887309
RHF/6-31G(d)	-1604,495227	-1604,475315	-1604,447115
B3LYP/6-31G(d)//RHF/6-31G(d)	-1614,970867	-1614,953903	-1614,928637
B3LYP/6-311G(d,p)//RHF/6-31G(d)	-1615,328732	-1615,310560	-1615,286132
BLYP/6-31G(d)//RHF/6-31G(d)	-1614,249766	-1614,233132	-1614,209006
BLYP/6-311G(d,p)//RHF/6-31G(d)	-1614,637795	-1614,621728	-1614,598761

* Kcal/mol

Calculated barriers for the conversions C2 to C2(ent) and C2 to D3

	C2C2-C2		C2D3-C2	
	Hartrees	Kcal/mol	Hartrees	Kcal/mol
AM1		11,231927		23,113880
RHF/3-21G	0,022677	14,230074	0,049673	31,170082
RHF/6-31G	0,020414	12,810034	0,049788	31,241868
RHF/6-31G(d)	0,019912	12,494840	0,048112	30,190424
B3LYP/6-31G(d)//RHF/6-31G(d)	0,016965	10,645526	0,042230	26,499728
B3LYP/6-311G(d,p)//RHF/6-31G(d)	0,018172	11,402985	0,042600	26,731753
BLYP/6-31G(d)//RHF/6-31G(d)	0,016634	10,437822	0,040759	25,576520
BLYP/6-311G(d,p)//RHF/6-31G(d)	0,016066	10,081777	0,039034	24,493701

Calculated zero-point energies (unscaled) and thermal corrections to energy (including ZPE) at AM1 level

	ZPE	E(Ther)	Enthalpies
C2C2, 247 K	0,484898	0,505381	0,866354
C2, 247 K	0,485338	0,506297	0,849370
C2D3, 341 K	0,484733	0,524094	0,904300
C2, 341 K	0,485338	0,525588	0,868959

Calculated zero-point and thermal corrections to the barriers of conversion C2-C2(ent) and C2-D3

	DZPE	DE(Ther)	DH
C2C2-C2, 247 K	-0,00044	-0,00092	0,016984
C2C2-C2 (kcal/mol)	-0,27610	-0,57479	10,65746
C2D3-C2, 341 K	-0,00060	-0,00149	0,035341
C2D3-C2 (Kcal/mol)	-0,37964	-0,93749	22,1764775

Calculated zero-point energies and thermal corrections to energy (including ZPE) at AM1 level

	Zero-point energies	Thermal corrections to Energy
C2C2, 247 K	0,484898	0,505381
C2, 247 K	0,485338	0,506297
C2C3, 341 K	0,484733	0,524094
C2, 341 K/68 °C	0,485338	0,525588

Calculated zero-point and thermal corrections to the barriers of conversion C2-C2(ent) and C2-C3

C2C2-C2	-0,00044	-0,00092
C2C2-C2(kcal/mol)	-0,27610	-0,57479
C2C3-C2	-0,00060	-0,00149
C2C3-C2 (Kcal/mol)	-0,37964	-0,93749

C2, RHF/6-31G(d) geometry

	0	1	
C	0.000000000000	0.000000000000	0.000000000000
C	0.000000000000	0.000000000000	1.468279884148
C	1.229809886817	0.000000000000	2.236022782889
C	-1.203262036411	-0.062603837409	2.146197314244
C	-1.164003235874	-0.390470877459	3.556390504024
C	-0.031873566062	-1.022172977870	4.033492479110
C	1.241984064600	-0.631043364365	3.466050539111
C	2.434383293505	0.701485755190	1.774755451312
C	-2.463873673905	0.041579861179	1.383062135166
C	-2.192940074213	-0.080920602143	4.567133850640
C	2.514117551044	-0.728526547498	4.210730370164
C	-0.266796014056	-2.067772424812	5.047232119819
C	-3.722578619915	-0.283353032458	1.929356536203
C	-2.427289248740	0.430751929391	0.034218244920
C	-3.637508504911	0.708914920899	-0.629519555027
C	-4.848688382328	0.492663498218	-0.032481376748
C	-4.888309176375	-0.062021144383	1.247234040515
H	-3.783243373862	-0.723806096534	2.899738846867
H	-3.621701305539	1.079195741442	-1.634963260342
H	-5.828694321599	-0.316864498370	1.701707131322
H	-5.758806853664	0.707943087209	-0.563088845632
C	-1.160987004087	0.347673993429	-0.696129016538
C	1.121659497098	-0.430095101437	-0.738897811733
C	1.136011280753	-0.393613982846	-2.104983307918
C	0.015889591836	0.076605237945	-2.796481071895
C	-1.111591187267	0.419895401668	-2.103516060366
H	-1.981331600734	0.707981080312	-2.658699429595
H	0.022948441436	0.127498282485	-3.870572253808
H	1.981343633682	-0.802857823932	-0.220812444566
H	2.004012339173	-0.730846380997	-2.642217269243
C	-2.280241944292	-0.847304299514	5.733832792122
C	-2.948414365253	1.100667681823	4.478012614821
C	-3.798899858991	1.476280454170	5.485962634489
C	-3.919678390470	0.684289666356	6.628957374138
C	-3.164431781310	-0.454471467259	6.749263025796
H	-2.844857016649	1.727562601424	3.613708708550
H	-4.359231923070	2.389830941957	5.399706594024
H	-3.225354348615	-1.031455456081	7.652702371436
H	-4.580852999739	0.978969924605	7.424000655066
C	0.527297524464	-3.226870517979	5.074472764051
C	-1.409948116040	-2.017981706016	5.851518365230
C	-1.694487756223	-3.091461324758	6.708190268526
C	-0.887693726165	-4.200203004230	6.745912524039
C	0.227316275629	-4.272494068056	5.909371689438
H	0.843915440836	-5.153276102077	5.905485576380

H	1.372830456356	-3.301033013878	4.418487459521
H	-1.129501149390	-5.020763384354	7.397289500456
H	-2.578040313646	-3.064521631044	7.317644008927
C	2.365100980151	1.744444844043	0.827913983006
C	3.675563608009	0.400500772786	2.342419759954
C	4.827623980119	1.027947931972	1.825253642858
C	4.743707843690	1.978969977680	0.846593115418
C	3.489714217669	2.371240670079	0.369548761139
H	1.409494990387	2.061358265362	0.463491421729
H	5.793316542593	0.795730841033	2.226730413835
H	3.406429370425	3.165462527223	-0.350206156623
H	5.636625561461	2.452179017217	0.479056778145
C	3.718928316363	-0.394768318191	3.571034987930
C	2.583087181479	-1.096449101119	5.570228154528
C	3.777410618011	-1.301138952730	6.206545973748
C	4.973390450688	-1.136268781199	5.506998961249
C	4.936822601989	-0.668471622182	4.222474142311
H	5.864409771356	-0.489362558937	3.716730180576
H	5.916906291872	-1.332105885584	5.984105781048
H	1.685220502891	-1.214197506502	6.135286147306
H	3.787321189729	-1.588165918203	7.242563571308

C2C2 (TS-I), RHF/6-31G(d) geometry

0	1		
C	0.000000000000	0.000000000000	0.000000000000
C	0.000000000000	0.000000000000	1.464244188299
C	1.226303952804	0.000000000000	2.242660169419
C	-1.178750542297	0.090240415309	2.153047748861
C	-1.097580275479	0.177942220938	3.600620507985
C	-0.026075310010	0.869489456443	4.133251947441
C	1.247865597192	0.771938058280	3.388829564625
C	2.319772291806	-0.951779640707	1.997592355166
C	-2.448870847819	0.187401556674	1.430993549036
C	-1.948040835177	-0.624983250592	4.491487954614
C	2.606458473338	1.162094408675	3.849398512816
C	-0.240350904378	1.380106981027	5.512916701982
C	-3.649692976053	0.530516294774	2.087922402016
C	-2.474787272707	0.000510903019	0.042040567372
C	-3.720581757403	0.031846996039	-0.618475717139
C	-4.880774325499	0.302030844104	0.051672083522
C	-4.840798619550	0.583726024967	1.420554943270
H	-3.631147519928	0.759613996760	3.133661700364
H	-3.773504581152	-0.139732889157	-1.674568045652
H	-5.740455247071	0.846199761574	1.947349092406
H	-5.815242958240	0.325395276756	-0.479769735595
C	-1.213486361899	-0.095946819688	-0.695007658909
C	1.190534841405	0.160121779428	-0.740436395307
C	1.194688505581	0.122047576102	-2.106260399491
C	-0.005354831113	-0.070748376014	-2.797285381504
C	-1.179380210932	-0.162357393000	-2.103444100919
H	-2.089320236290	-0.268233874850	-2.658757028786
H	-0.011005874918	-0.118330984496	-3.871488292582
H	2.114689564598	0.319764770374	-0.223858907756
H	2.117279384972	0.245124572191	-2.644279905360
C	-1.846456837059	-0.468641563161	5.876832977448
C	-2.676084219831	-1.723980368476	3.993869338403
C	-3.300563026298	-2.605957492672	4.835549786656
C	-3.204503662752	-2.438845165249	6.217798818395
C	-2.481820468638	-1.390551939945	6.723762881299
H	-2.721699725144	-1.897982097046	2.938498665390
H	-3.842049183894	-3.440343687847	4.427413822667
H	-2.381584538795	-1.295720093938	7.787540030436
H	-3.675928092111	-3.139657021687	6.883171216913
C	0.224079655319	2.627897223144	5.952914959816
C	-1.101057130990	0.682880665567	6.380338150276
C	-1.311489492395	1.162248449973	7.681455054363
C	-0.752642096710	2.336143249856	8.116583474916
C	-0.008118392591	3.096392989395	7.222633541009
H	0.362322828500	4.064922388725	7.506994450768

H	0.702397594075	3.282627222014	5.266524608496
H	-0.939191439631	2.688738845099	9.114926595785
H	-1.965622166444	0.627489593221	8.341748384946
C	2.115911741076	-2.090848968527	1.193585943206
C	3.489969568027	-0.877343044679	2.758540957880
C	4.427572809832	-1.919733014129	2.686295546447
C	4.219644741409	-3.007372684491	1.879452055792
C	3.048247937841	-3.092048121473	1.125512467892
H	1.202806914036	-2.198370766442	0.645092122365
H	5.312482964321	-1.885067203866	3.291601241409
H	2.861721093813	-3.953547938426	0.509876203383
H	4.945490976695	-3.799882160951	1.845180909000
C	3.696537032417	0.315408124285	3.576963242593
C	2.905027558990	2.422626824114	4.386229361464
C	4.172136731581	2.776251817895	4.779899536518
C	5.221746385505	1.878498127643	4.625625586569
C	4.981561116504	0.680180322399	4.004317769837
H	5.810370760100	0.031783204563	3.798162813000
H	6.218154591954	2.140429760378	4.932829984065
H	2.152414709563	3.171691397781	4.419002518874
H	4.349494836874	3.759607574559	5.177003443448

C2D3 (TS-II), RHF/6-31G(d) geometry

	0	1	
C	0.000000000000	0.000000000000	0.000000000000
C	0.000000000000	0.000000000000	1.494398153769
C	1.199144530810	0.000000000000	2.340539279331
C	-1.232647835019	0.289862217332	2.087591363755
C	-1.371344934353	0.289207231169	3.515937809145
C	-0.288354100743	-0.108517727691	4.265373731487
C	1.011293377489	0.124156929527	3.712352336545
C	2.637959114158	0.013513057838	1.916636141842
C	-2.399694535915	0.569123107249	1.221501425997
C	-2.512140928500	0.800727612923	4.321095948357
C	2.007423100763	0.831517616388	4.558580413364
C	-0.527768126127	-0.772709954092	5.553679687345
C	-3.718897342977	0.277122167300	1.592780693933
C	-2.176597620640	1.145050273189	-0.032097922074
C	-3.269933019832	1.648753459933	-0.752024938214
C	-4.555896882530	1.460478827412	-0.308508959874
C	-4.784569194389	0.711438579669	0.843256004177
H	-3.904804158316	-0.289664275876	2.482182258391
H	-3.117204432642	2.136886841155	-1.694377714295
H	-5.787833751144	0.478812100180	1.151356318449
H	-5.382103322143	1.838553246585	-0.883713087225
C	-0.880035582314	0.870335643760	-0.672703217172
C	0.736166411008	-0.863518856387	-0.816698268621
C	0.867200984176	-0.666389925631	-2.172733582811
C	0.229773069341	0.411587108382	-2.771672780927
C	-0.675047346439	1.134966529601	-2.031833552037
H	-1.280942533732	1.867010756456	-2.529123178746
H	0.363868042825	0.619069809996	-3.817973804312
H	1.143581562604	-1.752361087883	-0.393395281543
H	1.453027230364	-1.351589084299	-2.758471290666
C	-2.724001148396	0.307332502380	5.614615314000
C	-3.255679947810	1.921144055641	3.912921350480
C	-4.240097447754	2.455754310871	4.704880947987
C	-4.515225368282	1.895910239547	5.951348902412
C	-3.752340411822	0.849046343453	6.400736493950
H	-3.038554658913	2.386358719176	2.973645472167
H	-4.785313802710	3.318140142040	4.365665092962
H	-3.914220673686	0.473517084777	7.393046573193
H	-5.287707290693	2.308720801427	6.575025746705
C	0.420686627328	-1.662585947993	6.081942898369
C	-1.784491620888	-0.678158263751	6.158054653218
C	-2.065769779625	-1.476782949843	7.274236038908
C	-1.123569348163	-2.336269156162	7.784078924697
C	0.132992245924	-2.426495164517	7.185152336866
H	0.868589257417	-3.108331761563	7.572146259887

H	1.375927710664	-1.760914986827	5.602452480172
H	-1.360531807272	-2.948430180612	8.635710616330
H	-3.037387624226	-1.436261466765	7.728984155286
C	3.167904661710	-0.766018106870	0.879550843139
C	3.579502409523	0.728537781694	2.681640784676
C	4.917119550496	0.793947176967	2.265090612679
C	5.370076920264	0.115024044076	1.163921473889
C	4.485142715518	-0.713637094007	0.491943266881
H	2.561511414883	-1.485623280316	0.401582723536
H	5.625837456747	1.344633461282	2.849728874116
H	4.823711982974	-1.340986446230	-0.313077657500
H	6.403338366392	0.175844772428	0.873158781348
C	3.197080848294	1.278259057718	3.980884463154
C	1.686333274887	1.309627737777	5.845919591270
C	2.513305157734	2.163319627194	6.527588893944
C	3.689808469736	2.616643523093	5.935138746051
C	4.014266561525	2.183621979514	4.677803062766
H	4.902276446809	2.566710844125	4.215914200487
H	4.327865147033	3.312798289543	6.449298374030
H	0.764866818129	1.037773675878	6.310972278503
H	2.230000162936	2.506513322114	7.506319712488