Supporting Information

A Computational Study of the Isomerization Reactions of Borirane

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I. Absolute energies

Table S1. Electronic and zero-point vibrational energy corrected energies (in atomic units) of stationary points computed at the B3LYP/6-311+G** level of theory along with number of imaginary vibrational frequencies (NIMAG), and single point energies at various levels of theory.

	6-311+G**			cc-pVTZ				cc-pVQZ			
Method	(U)B3LYP			CCSD(T)	CAS	MRCI	MRCI+Q	CCSD(T)	CAS	MRCI	MRCI+Q
	E/a.u.	E+ZPVE/a.u.	NIMAG	E/a.u.	E/a.u.	E/a.u.	E/a.u.	E/a.u.	E/a.u.	E/a.u.	E/a.u.
borirane	-104.03936	-103.97664	0	-103.78647	-103.31366	-103.72083	-103.77397	-103.81668	-103.32046	-103.74709	-103.80265
A	-104.01248	-103.95110	0	-103.75995	-103.30645	-103.69980	-103.75094	-103.78859	-103.31308	-103.72474	-103.77813
A (trip., vert.)	-103.94680	n.a.	n.a.	-103.72172	-103.27402	-103.66278	-103.71213	-103.75030	-103.28060	-103.68775	-103.73931
B	-104.06043	-103.99793	0	-103.80789	-103.35318	-103.74711	-103.79733	-103.83710	-103.35979	-103.77259	-103.82509
C	-104.03263	-103.96973	0	-103.77864	-103.31366	-103.71462	-103.76687	-103.80847	-103.32033	-103.74054	-103.79519
D	-103.98265	-103.91844	0	-103.73757	-103.27541	-103.67209	-103.72423	-103.76604	-103.28182	-103.69691	-103.75124
E	-104.05990	-103.99779	0	-103.80377	-103.33673	-103.73956	-103.79202	-103.83394	-103.34341	-103.76569	-103.82062
F (singlet)	-103.93940	-103.88217	0	-103.68577	-103.23167	-103.62262	-103.67398	-103.71504	-103.23865	-103.64809	-103.70175
F (triplet)	-103.93742	-103.88041	0	-103.68314	-103.23819	-103.62312	-103.67273	-103.71118	-103.24459	-103.64750	-103.69932
TS1	-104.01186	-103.95034	1	-103.75999	-103.30373	-103.69873	-103.75037	-103.78888	-103.31043	-103.72386	-103.77776
TS2	-103.98292	-103.92274	1	-103.72941	-103.24010	-103.65587	-103.71380	-103.75958	-103.24697	-103.68194	-103.74228
TS3	-103.96380	-103.90532	1	-103.70848	-103.22715	-103.63643	-103.69315	-103.73842	-103.23396	-103.66232	-103.72141
TS4	-103.97051	-103.91089	1	-103.71810	-103.23445	-103.64734	-103.70356	-103.74832	-103.24152	-103.67350	-103.73214
TS5	-103.95907	-103.89805	1	-103.71173	-103.22720	-103.63945	-103.69626	-103.74082	-103.23375	-103.66456	-103.72368
TS6	-103.95407	-103.89401	1	-103.70273	-103.22647	-103.63116	-103.68732	-103.73205	-103.23325	-103.65649	-103.71495
TS7	-103.94125	-103.87945	1	-103.69028	-103.21290	-103.61766	-103.67508	-103.71941	-103.21966	-103.64280	-103.70245
TS8	-103.95383	-103.89105	1	-103.69447	-103.22025	-103.62304	-103.67909	-103.72396	-103.22727	-103.64855	-103.70687
TS9	-103.98611	-103.92595	1	-103.72872	-103.26258	-103.66067	-103.71495	-103.75811	-103.26943	-103.68618	-103.74276
CH3BHCH (trip.)	-103.97613	-103.91628	0	-103.72079	-103.27282	-103.66015	-103.71022	-103.74866	-103.27920	-103.68443	-103.73666
TS10	-103.94597	-103.88903	1	-103.69606	-103.21732	-103.62621	-103.68185	-103.72561	-103.22412	-103.65183	-103.70982

II. Computed Harmonic Vibrational Frequencies and Infrared Intensities

Table S2. Harmonic vibrational frequencies (ω, in cm^{-1}) and infrared intensities (I, in km mol^{-1}) computed at the B3LYP/6-311+G** level of theory unless noted otherwise.

	Borirane		**A**			**B**		**C**		**D**		**E**	
Number	ω	I	ω	I	ω[a]	ω	I	ω	I	ω	I	ω	I
1	427.7	8.4	167.4	1.5	159.3	215.9	0.3	191.0	1.7	173.9	7.3	84.1	1.1
2	490.1	0.0	325.2	1.0	331.1	371.6	0.3	209.9	1.8	242.4	23.1	263.3	0.1
3	690.4	0.6	519.6	0.0	550.2	550.6	2.5	605.8	54.3	533.4	10.6	313.5	0.8
4	749.7	19.5	770.4	0.0	768.2	841.4	10.9	621.3	0.0	855.7	20.8	587.9	3.6
5	820.2	0.6	839.6	0.8	854.9	934.5	22.1	788.9	13.1	895.5	16.7	685.5	95.8
6	937.4	46.5	855.7	0.5	875.9	1024.3	41.6	925.8	7.5	935.4	19.7	792.7	4.0
7	949.2	44.4	963.2	0.0	945.9	1036.8	51.4	1007.0	24.6	1001.7	46.4	909.7	42.0
8	1013.6	31.2	965.1	51.6	952.0	1056.2	18.3	1050.8	0.5	1222.0	1.3	919.1	2.8
9	1029.0	16.0	1044.8	11.3	1051.5	1109.9	5.3	1176.2	1.1	1296.3	74.4	1310.9	13.5
10	1182.3	0.0	1104.8	10.6	1125.0	1246.9	42.9	1409.7	5.4	1396.6	26.3	1342.0	2.1
11	1192.1	18.9	1274.7	24.5	1316.2	1320.3	2.4	1487.8	5.2	1412.2	1.6	1435.4	9.1
12	1402.7	5.5	1482.4	17.0	1497.3	1450.4	58.5	1489.6	4.8	1503.5	13.5	1461.6	7.0
13	1430.4	21.9	1490.4	0.8	1510.1	1641.8	48.5	1583.5	21.1	1507.5	9.6	1668.1	219.2
14	2722.9	87.7	2589.9	147.2	2657.7	2568.2	128.8	2835.5	18.9	2960.0	13.7	3008.8	0.1
15	3089.4	7.5	3098.3	6.4	3151.2	2640.8	149.1	3013.0	49.3	2997.2	1.0	3066.1	8.6
16	3092.1	0.2	3098.8	22.4	3153.6	3108.1	21.1	3055.7	22.1	3039.7	25.7	3091.2	3.1
17	3147.8	0.0	3175.9	6.9	3243.7	3119.4	11.2	3058.8	7.2	3105.9	14.6	3132.3	10.3
18	3163.5	7.7	3176.3	23.7	3244.3	3194.9	14.4	3095.8	25.4	3106.2	20.2	3195.1	0.2

[a] CASPT2/cc-pVTZ

III. IRC for reaction borirane → **C**

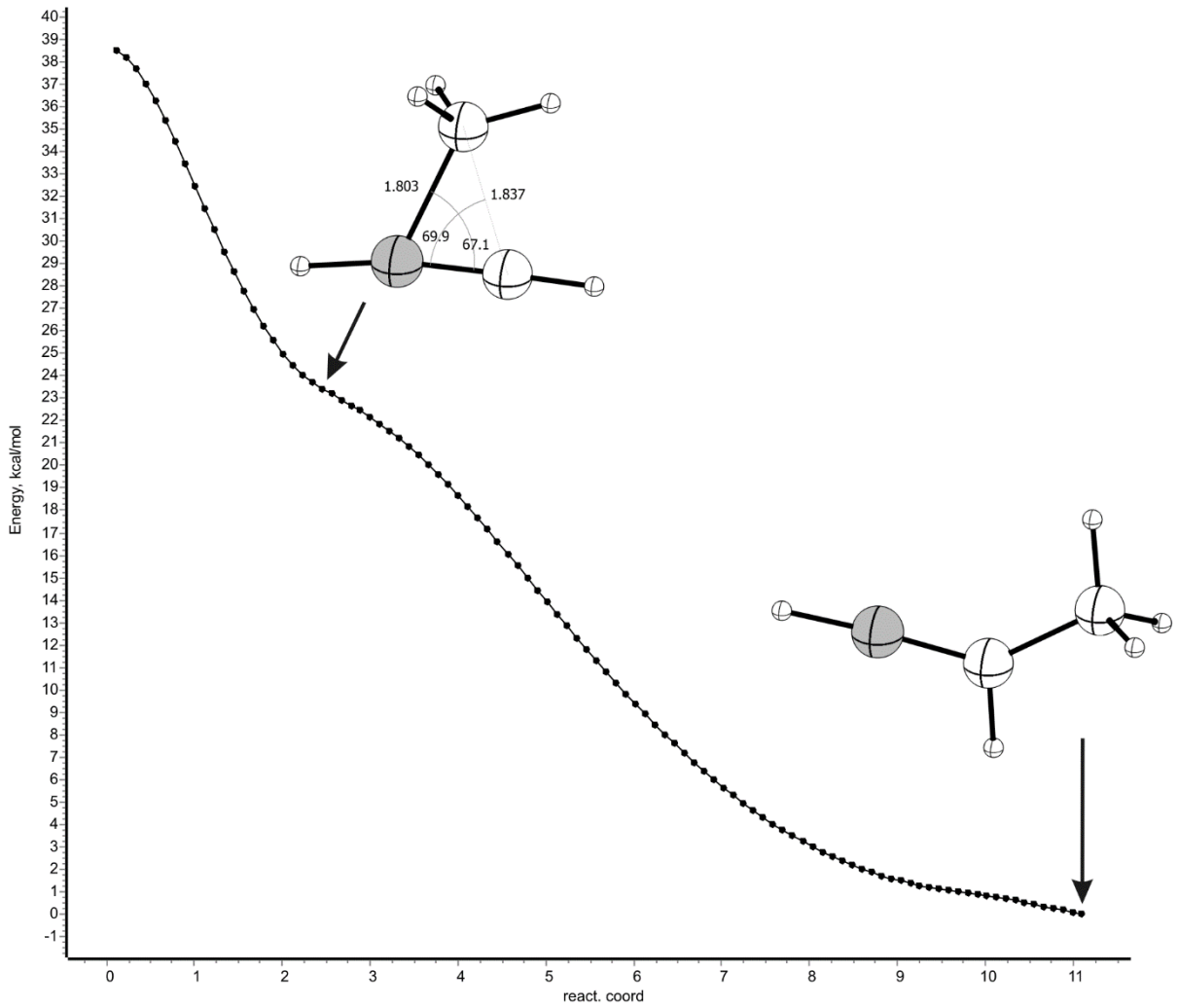

Figure S1. Forward reaction coordinate computed from **TS4** at the B3LYP/6-311+G** level of theory.

IV. Cartesian Coordinates of Stationary Points

All Cartesian Coordinates are given in Ångström.

B3LYP/6-311+G**

```
8
Borirane, C2v
6        0.000000000      0.776576000     -0.351702000
5        0.000000000      0.000000000      0.963766000
6        0.000000000     -0.776576000     -0.351702000
1        0.903278000      1.281915000     -0.685539000
1       -0.903278000      1.281915000     -0.685539000
1        0.903278000     -1.281915000     -0.685539000
1       -0.903278000     -1.281915000     -0.685539000
1        0.000000000      0.000000000      2.143749000

8
2-bora-propane-1,3-diyl, A, Cs
6       -0.000026000     -0.213091000      1.265881000
6       -0.000026000     -0.213091000     -1.265881000
5       -0.000026000      0.591992000      0.000000000
1       -0.000124000     -1.302662000      1.257093000
1        0.000230000      0.208100000      2.270081000
1       -0.000124000     -1.302662000     -1.257093000
1        0.000230000      0.208100000     -2.270081000
1        0.000226000      1.786259000      0.000000000

8
vinylborane, B
6       -0.023287000     -0.483942000      0.000039000
5        1.351570000      0.206638000     -0.000047000
6       -1.164262000      0.229235000     -0.000001000
1        2.367089000     -0.418505000     -0.000106000
1       -0.109069000     -1.569824000      0.000098000
1       -1.142859000      1.315628000     -0.000003000
1       -2.149006000     -0.232076000     -0.000156000
1        1.401288000      1.399826000      0.000173000

8
ethylideneborane, C
6        1.165333000     -0.185484000     -0.000002000
6       -0.232680000      0.391028000      0.000021000
5       -1.473391000     -0.210185000     -0.000060000
1        1.726691000      0.141542000     -0.881508000
1        1.726642000      0.141419000      0.881584000
1       -0.291034000      1.485046000      0.000008000
1       -2.547893000     -0.673185000      0.000162000
1        1.156630000     -1.277158000     -0.000064000

8
ethylborylene, D
6       -1.063391000     -0.188514000      0.000005000
6        0.345935000      0.450711000      0.000002000
5        1.516332000     -0.544428000     -0.000004000
1       -1.213064000     -0.814754000      0.881996000
1       -1.836374000      0.582303000      0.000122000
1        0.492845000      1.097961000      0.881207000
1        0.492817000      1.097976000     -0.881197000
1       -1.213150000     -0.814523000     -0.882146000

8
methyl methylideneborane, E
6       -1.403796000     -0.006789000      0.000008000
5        0.123100000     -0.023765000     -0.000011000
6        1.504328000      0.002069000      0.000000000
1       -1.840995000     -0.464853000     -0.891731000
1       -1.840954000     -0.464055000      0.892172000
1        2.108078000     -0.900666000      0.000027000
1        2.070030000      0.929255000      0.000001000
1       -1.714848000      1.047465000     -0.000462000

8
3-bora-1-propylidene singlet, F
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```
6        0.110097000     -0.535935000      0.094977000
6        1.270239000      0.246346000     -0.213209000
1        1.348312000      1.092849000      0.491239000
5       -1.206275000      0.306489000     -0.085755000
1       -2.197904000     -0.266300000     -0.404148000
1       -1.219003000      1.464137000      0.180976000
1       -0.229033000     -0.539991000      1.180719000
1        0.046985000     -1.545604000     -0.310617000

8
3-bora-1-propylidene triplet
6        0.055105000     -0.509255000      0.015776000
6        1.333693000      0.202430000     -0.019233000
1        1.610200000      1.247865000     -0.082564000
5       -1.263620000      0.338359000     -0.019697000
1       -2.300552000     -0.229197000     -0.183357000
1       -1.262667000      1.517121000      0.156523000
1       -0.065957000     -1.075420000      0.967809000
1        0.004284000     -1.311214000     -0.739184000

8
TS1
6       -0.021333000     -0.221256000      1.213201000
6       -0.021333000     -0.221256000     -1.213201000
5       -0.021333000      0.647897000      0.000000000
1       -0.359127000     -1.256045000      1.183744000
1        0.417858000      0.058850000      2.170656000
1       -0.359127000     -1.256045000     -1.183744000
1        0.417858000      0.058850000     -2.170656000
1        0.245195000      1.809973000      0.000000000

8
TS2
6       -0.829575000     -0.312490000      0.058044000
5        0.848179000     -0.470204000     -0.001223000
6        0.082837000      0.764357000     -0.187334000
1       -1.480989000     -0.367322000      0.929427000
1       -1.204872000     -0.819045000     -0.826518000
1        0.101449000      1.822732000      0.042963000
1        1.272829000      0.399652000      0.801396000
1        1.551114000     -1.396199000     -0.165410000

8
TS3
6       -0.068303000      0.797982000      0.007670000
5       -0.875195000     -0.410604000     -0.062739000
6        0.786882000     -0.396410000     -0.025849000
1       -0.998382000     -0.267410000      1.182516000
1        0.132634000      1.866647000     -0.061639000
1        1.274901000     -0.779104000      0.863420000
1        1.467530000     -0.381617000     -0.881520000
1       -1.812185000     -0.794928000     -0.680009000

8
TS4
6       -0.808138000     -0.522393000     -0.102975000
5       -0.397009000      0.832496000     -0.031058000
6        0.911828000     -0.055087000      0.034768000
1        0.347168000     -1.160845000     -0.218981000
1       -1.268409000     -1.243847000      0.560529000
1        1.521698000     -0.155599000     -0.861635000
1        1.466103000     -0.095080000      0.972539000
1       -0.703657000      1.957770000      0.112075000

8
TS5
6        0.852534000     -0.116328000      0.000039000
5       -0.665865000      1.029755000      0.000120000
6       -0.566513000     -0.543705000      0.000025000
1        1.428219000     -0.208937000      0.915026000
1        1.428562000     -0.209570000     -0.914662000
1       -0.947887000     -1.024310000      0.897336000
1       -0.947582000     -1.023133000     -0.898102000
1        0.651880000      1.277372000     -0.000578000

8
TS6
6        1.114175000     -0.147467000      0.005670000
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6       -0.298150000      0.367844000     -0.051450000
5       -1.538668000     -0.370462000     -0.153464000
1        1.607466000      0.071280000     -0.946853000
1        1.692907000      0.340252000      0.793318000
1       -0.428345000      1.456617000     -0.043020000
1       -1.218675000     -0.109070000      1.086431000
1        1.143841000     -1.229029000      0.152125000

8
TS7
6        1.013646000      0.174204000     -0.000012000
6       -0.986679000      0.264146000     -0.000028000
5       -0.334947000     -1.027392000      0.000091000
1        1.540801000     -0.156353000     -0.892179000
1        0.969196000      1.270193000     -0.000112000
1       -1.268924000      0.774522000     -0.920078000
1       -1.268930000      0.774688000      0.919929000
1        1.540790000     -0.156190000      0.892222000

8
TS8
6       -1.112027000     -0.331182000      0.000019000
5       -0.053087000      0.701664000      0.000044000
6        1.184719000     -0.149147000     -0.000063000
1       -1.037324000     -1.411746000      0.000841000
1       -2.129891000      0.061237000     -0.000573000
1        1.615480000     -0.575504000      0.908131000
1        1.614401000     -0.575955000     -0.908561000
1       -0.233384000      1.875621000      0.000210000

8
TS9 (HC-BH-CH3, singlet)
6       -1.331499000     -0.227962000     -0.000002000
5       -0.233650000      0.606152000      0.000001000
6        1.166160000     -0.222661000      0.000000000
1       -2.117025000     -0.961892000      0.000013000
1       -0.248726000      1.796945000      0.000002000
1        1.068202000     -1.308625000     -0.000055000
1        1.728927000      0.073316000     -0.889653000
1        1.728903000      0.073234000      0.889705000

8
HC-BH-CH3, triplet minimum
6       -1.502650000     -0.145724000      0.000017000
1       -2.013630000     -1.101369000     -0.000030000
5       -0.163124000      0.547834000     -0.000047000
1       -0.142703000      1.745357000      0.000004000
6        1.208415000     -0.226643000     -0.000009000
1        1.134786000     -1.316110000     -0.000448000
1        1.801618000      0.083894000     -0.870893000
1        1.800959000      0.083257000      0.871559000

8
TS10
6        0.436895000      0.687305000     -0.035141000
6        0.435841000     -0.687807000     -0.035060000
1        1.213624000     -1.414465000     -0.269713000
5       -1.043645000      0.000477000     -0.000398000
1       -1.668953000      0.001125000      1.014026000
1       -1.606549000     -0.000035000     -1.056516000
1        1.215296000      1.412627000     -0.271713000
1        0.828393000      0.001373000      1.007114000
```

CASPT2/cc-pVTZ:

```
8
compound A
C     1    6        -0.0000036908       -0.2132006670        1.2612610692
C     2    6        -0.0000036937       -0.2132006949       -1.2612610507
B     3    5        -0.0000057117        0.6077782168       -0.0000000156
H     4    1        -0.0001679278       -1.2977929117        1.2232230274
H     5    1         0.0002833210        0.1886584081        2.2683372893
H     6    1        -0.0001679496       -1.2977929317       -1.2232230590
H     7    1         0.0002833344        0.1886584403       -2.2683372265
H     8    1         0.0001423183        1.7998371401       -0.0000000341
```