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On the 3D → 2D isomerisation of hexaborane(12)

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SUPPLEMENTARY INFORMATION (6 pages)

All computations in this work were carried out with the M06-2X/aug-cc-pVDZ level of theory. The stationary points were checked with frequency computations, with one imaginary frequency for the transition states (TS_i) and zero imaginary frequencias for reactant (R), product (P) and intermediates (I_j).

In Table S1, we display the four *styx* isomers of hexaborane(12), B_6H_{12}. Given a borane B_pH_{p+q}, in *styx* notation, *s* stands for number of bridge hydrogens, *t* for the number of three-center B-B-B bonds, *y* for the number of two-center B-B bonds and *x* for the number of BH_2 groups [1]. As shown in Table S1, the lowest energy isomer is the known isomer 4212, labeled as reactant (R) in the 3D → 2D isomerisation process. This structure has C_2 symmetry and has been determined experimentally. The product (P) of the isomerisation is isomer 6030, planar haxaborane(12) with D_{3h} symmetry. This isomer is structurally equivalent to benzene, and lies 100 kJ·mol^{-1} above R. The 5121 isomer turns out to be intermediate I_2 in the isomerisation process as shown in Figure 2, and lies 104 kJ·mol^{-1} above R. Finally, isomer 3303, with a pentagonal pyramid structure, lies only 13 kJ·mol^{-1} above R.

The description of the Tables in this Supplementary Information file is described below:

Table S1. The four *styx* isomers of hexaborane(12), B_6H_{12}, with their structures, Lipscomb's valence structures, relative energies ΔE(kJ·mol^{-1}) referred to lowest energy isomer R (*styx* 4212), and the labels according to stationary points (SP) in the main text.

Table S2. Selected B-B distances (Å) for the stationary points from Figure 2 of the main text.

Table S3. Selected B-H distances (Å) for the stationary points from Figure 2 of the main text.

Tables S4-S11. Cartesian coordinates (Å) for the optimised geometries of the stationary points considered in this work, displayed in Figure 2 of the main text, and of *styx* isomer 3303.

Table S1. The four *styx* isomers of hexaborane(12), B_6H_{12}, with their structures, Lipscomb's valence structures, relative energies ΔE(kJ·mol^{-1}) referred to lowest energy isomer R (*styx* 4212), and the labels according to stationary points (SP) in the main text.

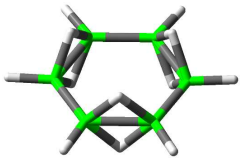
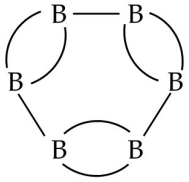
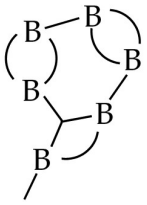
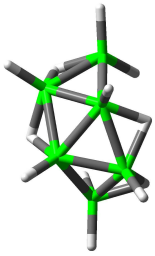
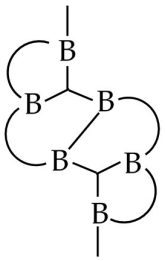
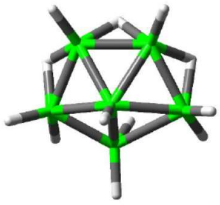
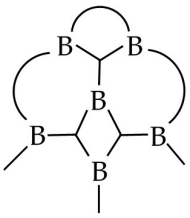
Styx	Label	ΔE	Structure	Lipscomb's notation [1]
6030	P	100.1		
5121	I_2	103.7		
4212	R	0.0		
3303	---	12.6		

Table S2. Selected B-B distances (Å) for the stationary points from Figure 2 of the main text. Bold numbers refer to distances with major changes.

B(*i*)-B(*j*)	R	TS_1	Int_1	TS_2	Int_2	TS_3	P
1-2	1.737	1.742	1.754	1.730	1.777	1.780	1.798
1-3	1.904	1.881	1.835	1.669	1.708	1.708	1.714
2-3	**1.724**	**1.744**	**1.734**	**2.395**	**2.778**	**2.935**	**3.042**
2-4	1.797	1.758	1.749	1.725	1.700	1.698	1.714
3-4	**1.788**	**1.720**	**1.763**	**2.434**	**2.822**	**3.385**	**3.512**
3-5	1.797	1.870	1.876	1.991	1.786	1.782	1.798
4-5	**1.724**	**1.763**	**1.717**	**1.873**	**1.885**	**2.800**	**3.042**
4-6	1.904	1.698	1.867	1.714	1.735	1.917	1.798
5-6	1.737	1.974	1.741	1.888	1.843	1.713	1.714

Table S3. Selected B-H distances (Å) for the stationary points from Figure 3 of the main text. Bold numbers refer to distances with major changes.

B(*i*)-H(*j*)	R	TS_1	Int_1	TS_2	Int_2	TS_3	P
1-7	1.193	1.194	1.195	1.336	1.320	1.321	1.321
1-13	1.196	1.195	1.195	1.192	1.196	1.195	1.197
1-14	1.361	1.365	1.378	1.305	1.314	1.341	1.321
2-7	**2.442**	**2.425**	**2.391**	**1.352**	**1.334**	**1.312**	**1.321**
2-8	1.186	1.187	1.186	1.200	1.198	1.200	1.197
2-14	1.298	1.302	1.307	1.349	1.338	1.307	1.321
2-15	**1.367**	**1.346**	**1.401**	**2.261**	**2.464**	**2.543**	**2.573**
3-9	1.187	1.186	1.188	1.190	1.194	1.196	1.197
3-11	**2.583**	**2.514**	**2.789**	**2.221**	**1.324**	**1.320**	**1.321**
3-18	1.289	1.285	1.320	1.313	1.366	1.310	1.321
4-10	1.187	1.222	1.190	1.293	1.304	1.294	1.321
4-15	1.289	1.323	1.308	1.207	1.206	1.192	1.197
4-16	**2.512**	**2.384**	**2.665**	**2.438**	**2.529**	**2.092**	**1.321**
5-11	1.186	1.191	1.265	1.190	1.313	1.323	1.321
5-17	1.298	1.213	1.190	1.207	1.195	1.201	1.197
5-18	1.367	1.383	1.332	1.365	1.298	1.327	1.321
6-10	**2.717**	**1.822**	**2.166**	**1.361**	**1.325**	**1.354**	**1.321**
6-12	1.193	1.188	1.193	1.197	1.203	1.204	1.197
6-16	1.196	1.194	1.193	1.192	1.194	1.211	1.321
6-17	**1.361**	**2.286**	**2.592**	**2.210**	**2.245**	**2.425**	**2.573**

Table S4. Cartesian coordinates (Å) of reactant R, hexaborane(12) with C_2 symmetry, *styx* isomer 4212.

Atom	X	Y	Z
B	1.739776	-0.399648	-0.780911
B	1.154539	0.873589	0.244717
B	0.574313	-0.685096	0.697929
B	-0.574313	0.685096	0.697929
B	-1.154539	-0.873589	0.244717
B	-1.739776	0.399648	-0.780911
H	2.913292	-0.567416	-0.646878
H	1.865799	1.490013	0.966944
H	0.946677	-1.244993	1.676296
H	-0.946677	1.244993	1.676296
H	-1.865799	-1.490013	0.966944
H	-2.913292	0.567416	-0.646878
H	1.178184	-0.852441	-1.734753
H	1.557626	0.932657	-0.987829
H	0.002626	1.533729	-0.082457
H	-1.178184	0.852441	-1.734753
H	-1.557626	-0.932657	-0.987829
H	-0.002626	-1.533729	-0.082457

Table S5. Cartesian coordinates (Å) of transition state TS_1.

Atom	X	Y	Z
B	-2.061837	0.293779	-0.485473
B	-1.062255	-1.010090	0.092409
B	-0.632059	0.564801	0.706538
B	0.618260	-0.560012	0.346892
B	0.966318	1.110363	-0.096332
B	2.169767	-0.436180	-0.330771
H	-3.166143	0.187525	-0.043963
H	-1.479458	-1.874082	0.791134
H	-0.857283	0.945544	1.807423
H	1.329749	-1.236237	1.073922
H	1.563217	1.788719	0.679938
H	3.127392	0.075580	0.151388
H	-1.871716	0.972805	-1.450400
H	-1.737522	-0.920840	-1.017667
H	0.067930	-1.367247	-0.544624
H	2.293565	-1.236273	-1.208046
H	1.098642	1.346993	-1.278132
H	-0.359347	1.504208	-0.127285

Table S6. Cartesian coordinates (Å) of intermediate I_1.

Atom	X	Y	Z
B	2.077076	0.542078	0.084775
B	1.137909	-0.926856	0.273719
B	0.521658	0.246933	-0.843751
B	-0.590147	-0.804045	0.032073
B	-0.829236	0.874972	0.297245
B	-2.290317	-0.032371	0.024503
H	3.151472	0.216083	-0.324180
H	1.622734	-1.958534	-0.055044
H	0.446652	0.160957	-2.026188
H	-1.082521	-1.756008	-0.485787
H	-1.940984	1.327349	-0.103741
H	-2.718706	-0.241576	-1.068831
H	1.953739	1.598825	0.629050
H	1.846607	-0.283728	1.163826
H	0.044887	-1.167108	1.116021
H	-2.984209	-0.130261	0.990359
H	-0.511913	1.29291	1.365151
H	0.037525	1.437536	-0.543458

Table S7. Cartesian coordinates (Å) of transition state TS_2.

Atom	X	Y	Z
B	-2.123996	0.129925	-0.203213
B	-1.062030	-1.147934	0.279609
B	-0.886693	1.226977	0.026143
B	0.543337	-0.730353	-0.193879
B	1.095914	1.049983	-0.015132
B	2.213387	-0.468399	0.089490
H	-2.008044	-0.481054	0.978656
H	-1.293482	-2.269514	0.636560
H	-1.023438	2.070106	0.854707
H	1.376674	-1.479111	0.450785
H	1.054230	1.604724	1.037046
H	2.722335	-0.121337	1.116282
H	-3.301272	0.269428	-0.331668
H	-1.791177	-0.960086	-0.839693
H	0.501541	-1.068479	-1.351953
H	2.894911	-0.788596	-0.834547
H	1.894466	1.539673	-0.775741
H	0.073659	1.383249	-0.855521

Table S8. Cartesian coordinates (Å) of intermediate I_2, *styx* isomer 5212.

Atom	X	Y	Z
B	1.924318	-0.016831	-0.181616
B	0.810237	-1.393517	-0.031784
B	0.967287	1.378643	0.049434
B	-0.720892	-0.845285	0.462391
B	-0.777492	1.011905	0.146179
B	-2.073518	-0.180214	-0.396695
H	1.332439	-0.770103	-1.089253
H	1.119740	-2.542546	-0.167530
H	1.286000	2.523921	0.165166
H	-1.656171	-1.427707	-0.234218
H	0.002389	1.343053	-0.856337
H	-2.045990	0.027105	-1.581598
H	3.092722	-0.066952	-0.432354
H	1.744551	-0.891113	0.783063
H	-0.962981	-1.001452	1.633229
H	-3.102863	-0.040858	0.191699
H	-1.563293	1.904634	0.262288
H	0.103758	1.168518	1.086298

Table S9. Cartesian coordinates (Å) of transition state TS_3.

Atom	X	Y	Z
B	1.842605	0.094030	-0.116172
B	0.941287	-1.438288	-0.034919
B	0.889017	1.492335	0.115190
B	-0.738076	-1.474647	0.212597
B	-0.883364	1.316624	0.051970
B	-1.920608	-0.023210	-0.199015
H	1.301738	-0.678314	-1.041603
H	1.507395	-2.483002	-0.204548
H	1.316773	2.589436	0.321675
H	-1.434442	-1.123770	-0.820101
H	0.020847	1.590695	-0.873676
H	-2.731396	0.201914	-1.060037
H	3.021326	0.064809	-0.313408
H	1.605861	-0.777226	0.875549
H	-1.264133	-2.300499	0.892922
H	-2.489859	-0.475884	0.769465
H	-1.506302	2.320802	0.265284
H	-0.002115	1.236821	1.040224

Table S10. Cartesian coordinates (Å) of product P, planar hexaborane(12) with D_{3h} symmetry, *styx* isomer 6030.

Atom	X	Y	Z
B	-0.856967	1.532848	0.000000
B	-1.755969	-0.024269	0.000000
B	0.856967	1.532848	0.000000
B	-0.899002	-1.508579	0.000000
B	1.755969	-0.024269	0.000000
B	0.899002	-1.508579	0.000000
H	-1.332035	0.769051	0.967970
H	-2.950645	0.043919	0.000000
H	1.513357	2.533374	0.000000
H	0.000000	-1.538102	0.967970
H	1.332035	0.769051	0.967970
H	1.437288	-2.577293	0.000000
H	-1.513357	2.533374	0.000000
H	-1.332035	0.769051	-0.967970
H	-1.437288	-2.577293	0.000000
H	0.000000	-1.538102	-0.967970
H	2.950645	0.043919	0.000000
H	1.332035	0.769051	-0.967970

Table S11. Cartesian coordinates (Å) of *styx* isomer 3303.

Atom	X	Y	Z
B	-0.685241	1.298205	-0.205303
B	1.044101	1.038809	-0.225625
B	0.010287	-0.002991	0.759258
B	-0.373822	-1.448331	-0.306239
B	-1.615672	-0.180774	0.134960
B	1.590409	-0.636165	0.123709
H	0.174923	1.345236	-1.230226
H	-1.684907	0.707007	-0.865570
H	1.793743	0.238627	-0.919203
H	-1.044683	2.384002	0.109717
H	1.637185	2.011335	0.108541
H	0.027293	0.081484	1.944613
H	-2.499843	-0.001029	0.908820
H	-1.822543	-1.175888	-0.568280
H	-0.474889	-2.535543	0.175611
H	-0.141198	-1.343037	-1.478806
H	2.434299	-0.440421	0.950924
H	1.750315	-1.615539	-0.539943

References

[1] Lipscomb, W.N. Topologies of B_6 and B_7 hydrides. *J. Phys. Chem.* **1961**, *65*, 1064-1066.