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Macropolyhedral boron-containing cluster chemistry. The $\{S_2B_{18}\}$ system. The reversible disassembly and reassembly of the hexagonal pyramidal $\{B_7\}$ feature in the $[S_2B_{18}H_{19}]^-$ anion. An establishment of molecular structures, intermediates and transition states by the DFT-structure / GIAO-NMR method.

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Data for deposition

Isolation of the $[S_2B_{18}H_{19}]^-$ anion 1 (after reference 15, reproduced here for convenience of reference)

syn-$B_{18}H_{22}$ (360 mg, 1.64 mmol) in thf (25 ml) was deprotonated with excess NaH, and elemental sulphur (400 mg; 12.5 mgatom) was added. The mixture was stirred for twelve hours, and then heated at reflux for three hours. Water was added, and the thf evaporated (water pump), and the solution was then filtered, and precipitated with a slight excess of $[N(PPh_2)_2]Cl$. The pale yellow precipitate, the $[N(PPh_2)_2]^+$ salt **1a** of the yellow anion $[S_2B_{18}H_{19}]^-$ (anion **1)**, was purified by column chromatography (silica gel, $CHCl_3$), R_F (analytical TLC, silufol, CH_2Cl_2), yield 48%. The other principal product was the well recognized [*nido*-7-$SB_{10}H_{11}]^-$ anion. Compound **1a** was characterised by single-crystal *X*-ray diffraction analysis (Figure 1, CCDC 186/1101, reference 15) and NMR spectroscopy. ^{11}B and ^1H NMR data for anion **1** (formally the *nido*-9′-thiaundecaborano-(7′,8′:5,6)-*iso*-(11_{6kc}<*VII*>)-*arachno*-11-thiaundecaboranate(1−) anion); $[PPh_4]^+$ salt, CD_3CN, 294-297 K {ordered as: tentative assignment $\delta(^{11}B)$ in ppm relative to Ξ 32.083971 MHz [$\delta(^1H)$ of directly attached hydrogen in square brackets]} are as follows: BH(2′) +16.5 [+3.81], BH(4′) +3.0 [+3.43], BH(10′) +1.9 [+2.83], BH(1) +0.9 [+3.91], B(5) *ca.* −3.9 [*conjuncto* position], BH(5′) *ca.* −3.9 [+2.74], BH(9) −8.6 [+3.13], B(6) −14.8 [*conjuncto* position], BH(8) −15.3 [+2.33], BH(10) −15.8 [+2.28], BH(11′) -17.6 [+1.13], BH(6′) −21.1 [+1.51], BH(3′) −23.2 [−0.38], BH(1′) −23.6 [+1.805], BH(7) *ca.* −47.4 [+0.52], BH(4) −47.4 [+ 0.11], BH(2) −48.7 [+0.37], BH(3) −49.7 [+0.15], with μH(7,8), (4,10) and (10′,11′) at $\delta(^1H)$ −1.45, −1.70 and −1.79 respectively; assignments by homo- and hetero-nuclear ^{11}B and ^1H NMR experiments. See also Table 1 in the paper for a summary of the $\delta(^{11}B)$ values.

Calculated coordinates

DFT B3LYP/6-31G* calculated coordinates for the $[S_2B_{18}H_{19}]^-$ anion **1** (isomeric with fluxional anion **5**)

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anion **1**: XYZ Angstrom coordinate file.

H	-3.16156	-0.02553	-2.52182
H	-0.14732	0.03654	-2.36164
S	3.15111	0.06732	-1.77608
H	-1.72343	2.49977	-1.52474
B	-2.58693	-0.01818	-1.47757
H	-1.68953	-2.48661	-1.39886
B	-0.81507	0.00028	-1.37335
H	3.41760	-2.42870	-0.89545
B	-1.73323	1.44048	-0.98865
H	1.47808	-1.75129	-0.96823
H	3.40723	2.49884	-0.72882
H	1.47620	1.84655	-0.86933
B	-1.70026	-1.43798	-0.83033
B	2.76354	-1.47697	-0.60294
B	2.75468	1.52509	-0.51405
H	-4.28665	1.54904	-0.19007
H	-4.28481	-1.49230	-0.15255
B	-3.31188	0.87088	-0.16516
B	-3.25883	-0.89267	-0.05066
B	3.69409	0.00522	0.10878
H	4.86415	0.01042	0.32337
B	-0.34357	-0.87173	0.10633
B	-0.31909	0.83663	0.10998
B	1.17453	-1.71478	0.28697
B	1.15357	1.69648	0.37377
H	1.05889	-2.83077	0.70001
H	1.03352	2.77530	0.88047
B	-1.90334	-1.49963	0.92269
B	2.56803	-0.91864	1.06261
S	-1.89457	1.63676	1.05020
B	2.54728	0.85918	1.11129
B	0.93732	-0.06266	1.20630
B	-2.87740	-0.04507	1.43986
H	-2.00698	-2.54847	1.48150
H	-1.70988	-0.64463	1.84898
H	3.03936	-1.48361	2.00231
H	2.99906	1.38272	2.08420
H	-3.61872	0.04654	2.36563
H	0.53167	-0.07102	2.33314

DFT B3LYP/6-31G* calculated coordinates for neutral $[S_2B_{18}H_{20}]$ (compound **4**)

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neutral **4**: XYZ Angstrom coordinate file.

H	3.25887	-0.04510	-2.63343
H	-3.08122	-0.89977	-2.35440
H	-0.47671	0.32147	-2.45785
H	-2.87540	2.07482	-1.90489
H	1.42045	-0.42009	-1.91796
H	1.28154	-2.34390	-1.66357
B	2.66947	-0.08562	-1.60594
B	-2.64114	-0.46793	-1.33979
B	-0.94773	0.25806	-1.36916
B	-2.50955	1.30135	-1.08215
H	-0.98467	-2.34422	-1.02056
B	1.50939	-1.36485	-1.03705
H	-1.19267	1.48358	-1.03639
S	2.15223	1.74954	-0.96288
H	-4.92522	0.25861	-0.36249

H	3.92567	-1.94179	-0.31565
B	-1.34680	-1.32345	-0.54290
H	4.62540	1.01186	-0.15987
B	3.07335	-1.11910	-0.23031
B	-3.75702	0.23166	-0.16431
B	3.53868	0.56179	-0.03222
H	-3.57008	-2.24688	0.32445
B	0.11285	-0.45444	0.05461
B	-2.91751	-1.25857	0.24019
B	0.62133	1.32155	0.17584
H	-0.04934	2.28098	0.35245
S	-3.00538	1.77666	0.73556
B	1.53893	-1.36143	0.69340
B	2.30046	1.40792	1.02079
H	1.30996	-2.39450	1.22858
B	-1.40560	-1.13241	1.18125
B	2.78262	-0.26461	1.30510
B	-2.82333	0.00009	1.51275
B	1.05475	0.22379	1.44722
H	2.59719	2.37836	1.62923
H	-1.50018	-0.01864	1.81612
H	-1.13090	-1.96608	1.97600
H	3.41494	-0.49296	2.28348
H	-3.40185	-0.09615	2.54425
H	0.59134	0.30919	2.53547

DFT B3LYP/6-31G* calculated coordinates for the lowest-energy form of the fluxional $[S_2B_{18}H_{19}]^-$ anion **5** (isomeric with anion **1**)

39
anion **5**: XYZ Angstrom coordinate file.

H	3.49302	-0.58472	-2.40314
H	-3.29420	-0.36191	-2.37491
H	-0.43717	0.31410	-2.49525
H	1.50468	-0.58065	-1.79571
H	-2.33433	2.43170	-1.57361
H	1.37035	-2.52289	-1.44620
B	2.83821	-0.32138	-1.44272
B	-2.68248	-0.19019	-1.36675
H	-1.31867	-2.38853	-1.32403
B	-0.94026	0.21475	-1.41897
S	2.71509	1.57841	-1.11476
B	-2.14194	1.41331	-0.99539
B	1.52697	-1.47637	-0.89972
B	-1.49276	-1.35604	-0.75885
H	0.06042	2.32050	-0.38529
H	-4.55244	1.10028	0.02230
B	-3.46861	0.61967	-0.04411
H	-3.96451	-1.88242	0.14360
B	-0.35868	1.26280	-0.05801
B	2.96239	-1.21735	0.07747
B	-0.05985	-0.59556	-0.04308
B	-3.07522	-1.08822	0.13417
H	3.70371	-2.13498	0.25550
B	3.63301	0.43800	0.18378
H	4.79702	0.62627	0.34493
B	2.21898	1.48298	0.76170
B	1.32716	-1.24273	0.82741
S	-2.09408	1.69809	1.00878
B	-1.57769	-1.45002	0.97382
H	2.43270	2.51389	1.32395

B	0.80554	0.44697	1.21956
B	2.52354	-0.09643	1.40988
H	1.05023	-2.20258	1.47530
H	-1.45766	-2.47488	1.56381
B	-2.65931	-0.12069	1.54581
H	-1.39042	-0.53563	1.84732
H	0.31693	0.59535	2.30504
H	-3.27185	-0.11801	2.56513
H	2.91096	-0.22737	2.53128

DFT B3LYP/6-31G* calculated coordinates for the transition state in the fluxionality of anion **5** (Figure **4**)

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ts for fluxionality of anion **5**: XYZ Angstrom coordinate file.

H	-3.02308	-0.13510	-2.52158
H	3.46233	-0.57214	-2.40819
H	-0.33701	0.61098	-2.37047
H	1.48432	-0.67703	-1.77560
H	-1.13344	-2.19517	-1.55733
B	2.80194	-0.33817	-1.44538
B	-2.55956	-0.04620	-1.42701
H	1.43884	-2.59986	-1.32718
H	-2.31725	2.55946	-1.26419
B	-0.82532	0.41274	-1.29511
S	2.53467	1.56359	-1.16821
B	-1.37846	-1.24612	-0.88253
B	1.56286	-1.52363	-0.83505
B	-2.14930	1.49887	-0.75079
H	-4.72394	0.81003	-0.23452
H	-3.80436	-2.04232	-0.28030
B	-3.57841	0.50904	-0.12949
B	-3.00784	-1.17349	-0.10005
H	4.72409	0.80972	0.23466
H	-0.00001	2.48951	0.00009
B	3.57851	0.50895	0.12954
B	3.00781	-1.17356	0.09996
B	-0.00021	1.30257	0.00015
H	3.80425	-2.04248	0.28011
B	-0.00004	-0.61510	0.00000
B	2.14943	1.49882	0.75086
B	-1.56294	-1.52373	0.83498
B	1.37841	-1.24619	0.88244
S	-2.53438	1.56356	1.16823
H	2.31737	2.55934	1.26440
H	-1.43900	-2.60013	1.32675
B	0.82528	0.41264	1.29512
B	-2.80202	-0.33826	1.44537
B	2.55958	-0.04633	1.42697
H	1.13327	-2.19531	1.55712
H	-1.48453	-0.67754	1.77594
H	-3.46255	-0.57211	2.40810
H	0.33716	0.61075	2.37059
H	3.02303	-0.13531	2.52156

DFT B3LYP/6-31G* calculated coordinates for transition state for reversion to anion **1** from the fluxional anion **5**

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Transition state from **5** to **1**: XYZ Angstrom coordinate file.

H	-3.37177	-0.59183	-2.32615
H	-0.38973	-0.15822	-2.45865

H	3.22104	-1.77282	-1.96956
H	-2.20682	2.21459	-1.94164
S	2.85322	0.83987	-1.68587
B	-2.73778	-0.32456	-1.35320
H	1.34254	-1.26532	-1.41356
B	-0.96748	-0.09931	-1.41826
B	2.67623	-1.04388	-1.19928
B	-2.03892	1.28724	-1.22084
H	-1.58248	-2.62628	-0.93804
B	-1.64948	-1.50053	-0.55624
H	-4.51859	1.27008	-0.20847
H	4.94467	0.10721	-0.09737
H	0.32829	1.87554	-0.36090
B	-3.47126	0.71279	-0.16428
H	1.00965	-2.81372	-0.20361
B	3.75541	0.14380	-0.09797
B	1.26082	-1.64883	-0.19043
B	-0.51792	1.04246	-0.16913
H	3.41451	2.65460	0.18463
B	2.75748	1.65849	0.11767
H	-4.14275	-1.69059	0.36380
B	-3.19261	-0.97800	0.25771
B	-0.27312	-0.63944	0.13252
B	2.81027	-1.25378	0.55106
S	-2.06247	1.83380	0.76275
H	3.42165	-2.14784	1.05235
B	1.30227	1.30943	0.97607
B	-1.69435	-1.24922	1.18627
B	2.73754	0.33467	1.29170
B	1.25753	-0.58572	1.24202
B	-2.80536	0.16073	1.53772
H	0.78050	1.96025	1.82555
H	-1.62550	-2.17742	1.93026
H	-1.56547	-0.21956	1.94162
H	3.14744	0.57247	2.38910
H	0.89065	-1.03792	2.28176
H	-3.48953	0.34428	2.49277