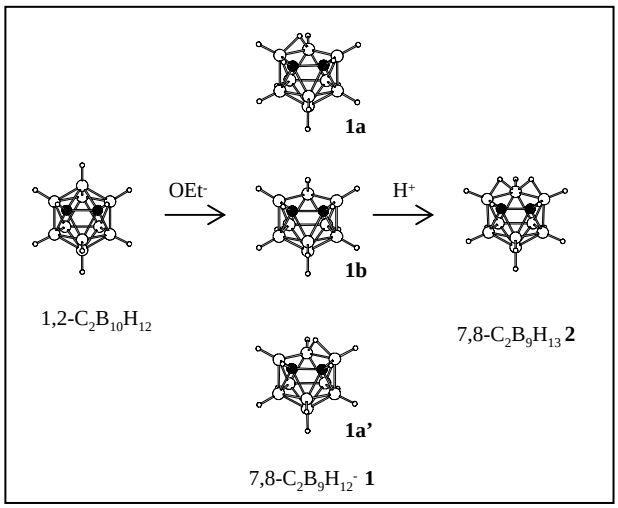
MOLECULAR STRUCTURES OF THE *NIDO*-CARBORANES $C_2B_9H_{12}^-$ and $C_2B_9H_{13}$

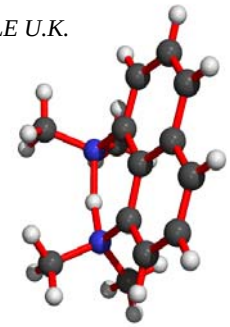
Mark A. Fox, Andrew K. Hughes, Andrew L. Johnson and Kenneth Wade
Chemistry Department, Durham University Science Laboratories, South Road, Durham, DH1 3LE U.K.

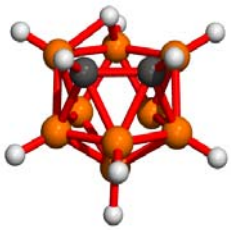
Experimental and theoretical studies were carried out on the long known *nido*-carborane anions, 7,8-, 7,9- and 2,9-$C_2B_9H_{12}^-$, (**1**, **3** and **5**) and the neutral *nido*-carboranes, 7,8- and 2,9-$C_2B_9H_{13}$, (**2** and **6**) to determine the positions of their *endo*/bridging hydrogens.

The black and white diagrams presented here were all generated from *ab initio* (HF/6-31G*) optimized geometries.

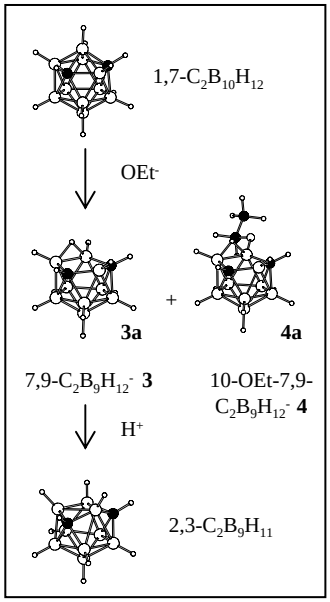
Good agreements between calculated boron-11 (and carbon-13) NMR chemical shift values generated from the optimized geometries with experimental solution state NMR data indicate that these geometries are present in solution.





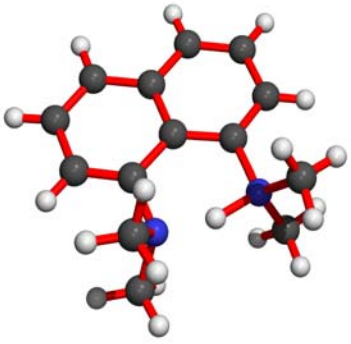


Crystal structure of 7,8-$C_2B_9H_{12}^-$ **1** with protonated proton sponge as cation

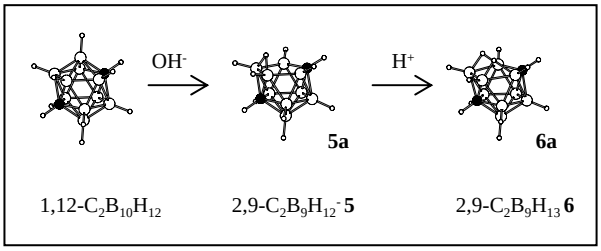


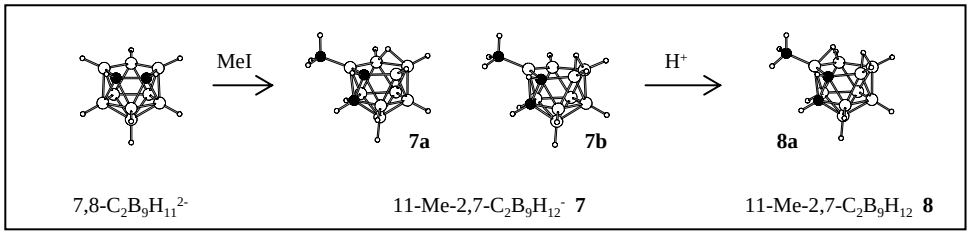
Theoretical (GIAO-HF/6-31G*//HF/6-31G*) and experimental ^{11}B and ^{13}C NMR data for carboranes **1-8**

	B1	B2	B3	B4	B5	B6	C7	C8	B9	B10	B11
7,8-$C_2B_9H_{12}^-$ **1**											
1a H at B10-B11	-36.65	-15.54	-15.90	-25.56	-1.42	-25.40	22.30	39.92	-8.82	-30.52	-14.20
1a/1a'	-36.65	-20.55	-15.90	-20.55	-13.41	-13.41	31.11	31.11	-11.51	-30.52	-11.51
Expt	*-37.2*	*-21.4*	*-16.4*	*-21.4*	*-15.9*	*-15.9*	42.2	42.2	*-10.4*	*-32.5*	*-10.4*
7,8-$C_2B_9H_{13}$ **2**											
2a	-28.97	8.65	-11.67	8.65	0.27	0.27	45.37	45.37	-25.07	-14.13	-25.07
Expt	*-26.8*	*4.6*	*-15.8*	*4.6*	*-3.9*	*-3.9*	63.5	63.5	*-26.8*	*-16.4*	*-26.8*
	B1	**B2**	**B3**	**B4**	**B5**	**B6**	**C7**	**B8**	**C9**	**B10**	**B11**
7,9-$C_2B_9H_{12}^-$ **3**											
3a	-32.53	-1.53	-19.44	-19.44	-1.53	-35.70	19.23	-5.65	19.23	-20.49	-20.49
Expt	*-33.9*	*-4.1*	*-21.1*	*-21.1*	*-4.1*	*-35.0*	*31.8*	*-5.5*	*31.8*	*-22.3*	*-22.3*
10-OEt-7,9-$C_2B_9H_{11}^-$ **4**											
4a	-33.83	-1.32	-25.20	-19.02	-1.08	-37.98	14.75	-7.54	19.67	-0.26	-26.15
Expt	*-36.8*	*-4.6*	*-29.1*	*-21.7*	*-4.6*	*-36.8*	*(26.3)*	*-8.3*	*(32.2)*	*0.4*	*-26.1*
	B1	**C2**	**B3**	**B4**	**B5**	**B6**	**B7**	**B8**	**C9**	**B10**	**B11**
2,9-$C_2B_9H_{12}^-$ **5**											
5a	-43.53	16.55	-14.44	-20.74	-20.74	-14.44	-27.57	-16.15	46.96	-16.15	-27.57
Expt	*-43.3*	*27.7*	*-19.6*	*-22.0*	*-22.0*	*-19.6*	*-28.9*	*-13.7*	*50.6*	*-13.7*	*-28.9*
2,9-$C_2B_9H_{13}$ **6**											
6a	-20.12	65.36	-37.41	-10.02	-10.02	-37.41	-21.85	-3.70	31.13	-3.70	-21.85
Expt	*-26.0*	*71.1*	*-35.3*	*-10.7*	*-10.7*	*-35.3*	*-25.5*	*-8.0*	45.7	*-8.0*	*-25.5*
	B1	**C2**	**B3**	**B4**	**B5**	**B6**	**C7**	**B8**	**B9**	**B10**	**B11**
11-Me-2,7-$C_2B_9H_{11}^-$ **7**											
7a	-43.87	28.31	-18.85	-12.54	-25.46	-9.65	38.75	-19.78	-15.92	-25.50	-10.53
7b	-38.72	33.86	-13.40	-34.32	-5.56	-20.13	14.89	-19.70	-19.80	-16.71	2.50
7a/7b	-41.30	31.09	-16.13	-23.43	-15.51	-14.89	26.82	-19.74	-17.86	-21.11	-4.02
Expt	*-43.8*	*40.6*	*-16.7*	*-22.0*	*-26.1*	*-14.6*	*47.4*	*-16.7*	*-19.8*	*-23.7*	*-7.5*
11-Me-2,7-$C_2B_9H_{12}$ **8**											
8a	-21.40	46.10	-5.52	-33.91	4.80	-30.38	17.95	-7.10	-2.14	-20.45	0.76
Expt	*-25.3*	58.6	*-9.0*	*-32.8*	*1.6*	*-29.0*	36.7	*-9.0*	*-7.7*	*-22.5*	*-0.1*



Crystal structure of 2,9-$C_2B_9H_{12}^-$ **5** with protonated proton sponge as cation





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