

Supplementary Information:

Solution and solid state studies on the binding of isomeric carboranes C2B10H12 by *p*-Bu^t-calix[5]arene

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General Remarks: All spectra were run on a DRX 300 MHz spectrometer using 99.8% chloroform-d₁ (CIL). No data could be collected for the calixarene signals as only concentration induced shifts were observed. Toluene-d₈ was not used as the residual methyl peak would cause signal overlap during the up field transition of the carborane B-H signals. Chloroform-d₁ was chosen over dichloromethane-d₂ as it is more readily available and will show similar C-H... π interactions with the calixarene cavity.

Job Plots: 10 mM solutions of host and guest were prepared in CDCl₃ and mixed in the ratio's stated. ¹H{¹¹B} NMR spectra of the mixtures were recorded and the chemical shift changes for the C-H (signal 1) and one B-H environment (signal 2) of the carborane were analyzed by Job's method to determine the host-guest stoichiometry.

NMR Titrations: A 4mM solution of guest was prepared in CDCl₃ and 800 μ L was added to an NMR tube fitted with a rubber septum. The titration solution was prepared in CDCl₃ and was 84 mM with respect to the host and 4 mM with respect to the guest to ensure a constant guest concentration throughout the experiment. The titration solution was added via syringe in the stated quantities and ¹H{¹¹B} MMR spectra were recorded. The chemical shift changes for the C-H (signal 1) and one B-H environment (signal 2) of the carborane were analyzed by non-linear regression methods to determine the association constants.

Competition Experiment: To an NMR tube was added 200 μ L of a 40 mM solution of each of the following, *o*-carborane, *m*-carborane, *p*-carborane and *p*-Bu^t-calix[5]arene in CDCl₃. A ¹H{¹¹B} NMR spectrum was obtained and the chemical shift of the C-H signal of each carborane was compared to its respect signal in 800 μ L of a 10 mM solution in CDCl₃. The C-H of *o*-carborane, *m*-carborane and *p*-carborane showed a shift of 0.1762, 0.0953 and 0.0065 ppm respectively indicating that all three species are bound at the same time in solution.

Job Plot 1: *p*-Bu^t-calix[5]arene and *o*-carborane

Host solution: 40.576 mg (5×10^{-5} mol) of *p*-Bu^t-calix[5]arene in 5 mL of CDCl₃

Guest solution: 14.423 mg (1×10^{-4} mol) of *o*-carborane in 10 mL of CDCl₃

Tube	V _{Host} [μL]	V _{Guest} [μL]	χ _{Guest}	1 [ppm]	χ * Δδ1 [ppm]	2 [ppm]	χ * Δδ2 [ppm]
0	800	0	0.0	0.0000	0.0000	0.0000	0.0000
1	720	80	0.1	3.3612	0.0188	2.0040	0.0119
2	640	160	0.2	3.3801	0.0338	2.0169	0.0213
3	560	240	0.3	3.4026	0.0440	2.0311	0.0277
4	480	320	0.4	3.4246	0.0498	2.0442	0.0317
5	400	400	0.5	3.4446	0.0523	2.0574	0.0330
6	320	480	0.6	3.4652	0.0504	2.0705	0.0317
7	240	560	0.7	3.4915	0.0404	2.0861	0.0261
8	160	640	0.8	3.5117	0.0300	2.1002	0.0186
9	80	720	0.9	3.5318	0.0157	2.1126	0.0097
10	0	800	1.0	3.5492	0.0000	2.1234	0.0000

NMR Titration 1: *p*-Bu^t-calix[5]arene and *o*-carborane

Guest solution: 5.769 mg (4×10^{-5} mol) of *o*-carborane in 10 mL of CDCl₃
 Titration solution: 68.168 mg (8.4×10^{-5} mol) of *p*-Bu^t-calix[5]arene in 1 mL of 4 mM
 guest solution

Sample	V _{Guest} [μL]	V _{Host} [μL]	meq of Host	Host [mM]	1 [ppm]	Δδ1 [ppm]	2 [ppm]	Δδ2 [ppm]
1	800	0	0.00	0.0000	3.5490	0.0000	2.1240	0.0000
2	800	10	0.25	1.0370	3.5254	0.0236	2.1093	0.0147
3	800	20	0.50	2.0488	3.5008	0.0482	2.0941	0.0299
4	800	30	0.75	3.0361	3.4791	0.0699	2.0797	0.0443
5	800	40	1.00	4.0000	3.4584	0.0906	2.0664	0.0576
6	800	50	1.25	4.9412	3.4381	0.1109	2.0538	0.0702
7	800	60	1.50	5.8605	3.4167	0.1323	2.0407	0.0833
8	800	80	2.00	7.6364	3.3740	0.1750	2.0142	0.1098
9	800	100	2.50	9.3333	3.3372	0.2118	1.9907	0.1333
10	800	120	3.00	10.9565	3.3015	0.2475	1.9684	0.1556
11	800	160	4.00	14.0000	3.2386	0.3104	1.9280	0.1960
12	800	200	5.00	16.8000	3.1811	0.3679	1.8940	0.2300
13	800	280	7.00	21.7778	3.0868	0.4622	1.8343	0.2897
14	800	400	10.00	28.0000	2.9775	0.5715	1.7669	0.3571
15	800	520	13.00	33.0909	2.8950	0.6540	1.7148	0.4092

K_a for signal 1: $6.4 \pm 0.3 \text{ M}^{-1}$ ($R^2 = 0.9999$)
 5.9 to 7.8 M⁻¹ for 95% confidence interval

K_a for signal 2: $6.8 \pm 0.3 \text{ M}^{-1}$ ($R^2 = 0.9999$)

6.2 to 7.4 M⁻¹ for 95% confidence interval

Job Plot 2: *p*-Bu^t-calix[5]arene and *m*-carborane

Host solution: 40.576 mg (5×10^{-5} mol) of *p*-Bu^t-calix[5]arene in 5 mL of CDCl₃

Guest solution: 14.423 mg (1×10^{-4} mol) of *m*-carborane in 10 mL of CDCl₃

Tube	V _{Host} [μL]	V _{Guest} [μL]	χ _{Guest}	1 [ppm]	χ * Δδ1 [ppm]	2 [ppm]	χ * Δδ2 [ppm]
0	800	0	0	0.0000	0.0000	0.0000	0.0000
1	720	80	0.1	2.8158	0.0097	2.5576	0.0080
2	640	160	0.2	2.8348	0.0155	2.5730	0.0128
3	560	240	0.3	2.8477	0.0194	2.5838	0.0160
4	480	320	0.4	2.8498	0.0250	2.5857	0.0206
5	400	400	0.5	2.8623	0.0251	2.5941	0.0216
6	320	480	0.6	2.8747	0.0226	2.6060	0.0187
7	240	560	0.7	2.8858	0.0186	2.6156	0.0151
8	160	640	0.8	2.8947	0.0142	2.6228	0.0115
9	80	720	0.9	2.9017	0.0096	2.6285	0.0078
10	0	800	1	2.9124	0.0000	2.6372	0.0000

NMR Titration 2: *p*-Bu^t-calix[5]arene and *m*-carborane

Guest solution: 5.769 mg (4×10^{-5} mol) of *m*-carborane in 10 mL of CDCl₃

Titration solution: 68.168 mg (8.4×10^{-5} mol) of *p*-Bu^t-calix[5]arene in 1 mL of 4 mM guest solution

Sample	V _{Guest} [μL]	V _{Host} [μL]	meq of Host	Host [mM]	1 [ppm]	Δδ1 [ppm]	2 [ppm]	Δδ2 [ppm]
1	800	0	0.00	0.0000	2.9109	0.0000	2.6384	0.0000
2	800	20	0.50	2.0488	2.8858	0.0251	2.6172	0.0212
3	800	40	1.00	4.0000	2.8612	0.0497	2.5972	0.0412
4	800	60	1.50	5.8605	2.8369	0.0740	2.5764	0.0620
5	800	80	2.00	7.6364	2.8156	0.0953	2.5593	0.0791
6	800	100	2.50	9.3333	2.7968	0.1141	2.5419	0.0965
7	800	120	3.00	10.9565	2.7757	0.1352	2.5260	0.1124
8	800	160	4.00	14.0000	2.7396	0.1713	2.4958	0.1426
9	800	200	5.00	16.8000	2.7073	0.2036	2.4690	0.1694
10	800	280	7.00	21.7778	2.6512	0.2597	2.4160	0.2224
11	800	400	10.00	28.0000	2.5859	0.3250	2.3686	0.2698
12	800	520	13.00	33.0909	2.5327	0.3782	2.3252	0.3132
13	800	640	16.00	37.3333	2.4887	0.4222	2.2900	0.3484
14	800	800	20.00	42.0000	2.4469	0.4640	2.2558	0.3826

Supplementary Material (ESI) for Dalton Transactions
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K_a for signal 1: $3.8 \pm 0.1 \text{ M}^{-1}$ ($R^2 = 1.000$)
3.5 to 4.1 M^{-1} for 95% confidence interval

K_a for signal 2: $4.6 \pm 0.3 \text{ M}^{-1}$ ($R^2 = 0.9997$)
3.9 to 5.5 M^{-1} for 95% confidence interval

Job Plot 3: *p*-Bu^t-calix[5]arene and *p*-carborane

Host solution: 40.576 mg (5×10^{-5} mol) of *p*-Bu^t-calix[5]arene in 5 mL of CDCl₃
Guest solution: 14.423 mg (1×10^{-4} mol) of *p*-carborane in 10 mL of CDCl₃

Tube	V _{Host} [μL]	V _{Guest} [μL]	χ _{Guest}	l [ppm]	χ * Δδl [ppm]
0	800	0	0.0	0.0000	0.0000
1	720	80	0.1	2.7369	0.0009
2	640	160	0.2	2.7376	0.0017
3	560	240	0.3	2.7387	0.0022
4	480	320	0.4	2.7399	0.0024
5	400	400	0.5	2.7402	0.0029
6	320	480	0.6	2.7419	0.0025
7	240	560	0.7	2.7437	0.0016
8	160	640	0.8	2.7442	0.0014
9	80	720	0.9	2.7451	0.0008
10	0	800	1.0	2.7460	0.0000