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Supporting Information

Molecular Recognition of Sialic Acid End Groups by Phenylboronates

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^{11}B NMR titration curves of PBA in methanol-water

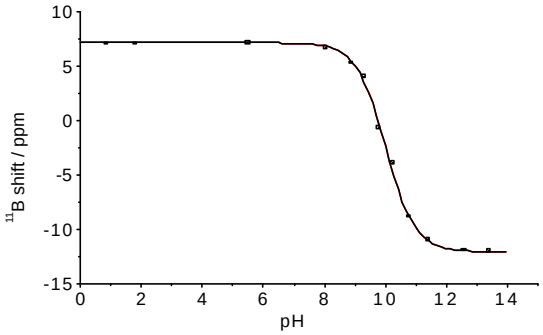

Figure 1S. pH profile of the ^{11}B chemical shift of a solution of PBA in a mixture methanol : water (1:2v/v,10% D_2O) at 96.3 MHz and 25 ^{o}C.

$$K_a = \frac{[PhB(OH)_3^-][H^+]}{[PhB(OH)_2]} = \frac{B^- \cdot H}{B^0}$$

The ^{11}B NMR spectra of PBA displayed a single resonance in the entire range of pHs studied (Figure 1S), which shows that phenylboronic acid (B^0) and the corresponding anion phenylboronate (B^-) are in fast exchange on the ^{11}B NMR time scale. The titration curve shows a jump in chemical shift from +9.4 to -6.0 ppm around pH 10, which can be ascribed to the ionization of B^0 to B^-.

The B-atom is planar (sp^2 hybridized) in B^0 and tetragonal (sp^3 hybridized) in B^-. These forms have chemical shifts that are around +9 and –16 ppm, respectively. If the exchange between B^0 and B^- is rapid on the ^{11}B NMR time scale, the averaged chemical shift and the ionization constant of PBA can be defined by Equations 1 and 2, respectively.

$$d = \sum_i c_i d_i \qquad (1)$$

$$K_a = \frac{[PhB(OH)_3^-][H^+]}{[PhB(OH)_2]} = \frac{B^- \cdot H}{B^0} \qquad (2)$$

Here c_i is the molar fraction of the B^0 or B^-, and d_i is the corresponding intrinsic chemical shift. Fitting of the experimental data to Equations1-2, gave a pKa value of 10.05 ± 0.03. This value is substantially higher than that determined for an aqueous solution of PBA (8.67),[17] which can be rationalized by the lower polarity of water-methanol as compared to water. The major aim of the present study is to elucidate the fashion of binding of PBA to hydroxycarboxylates. We assume that the structures are similar in water and in water-methanol. However, the formation constants may differ significantly for these media.

[17] J. O. Edwards, R. J. Sederstrom, *J. Phys. Chem.* **1961**, *65*, 862-863.

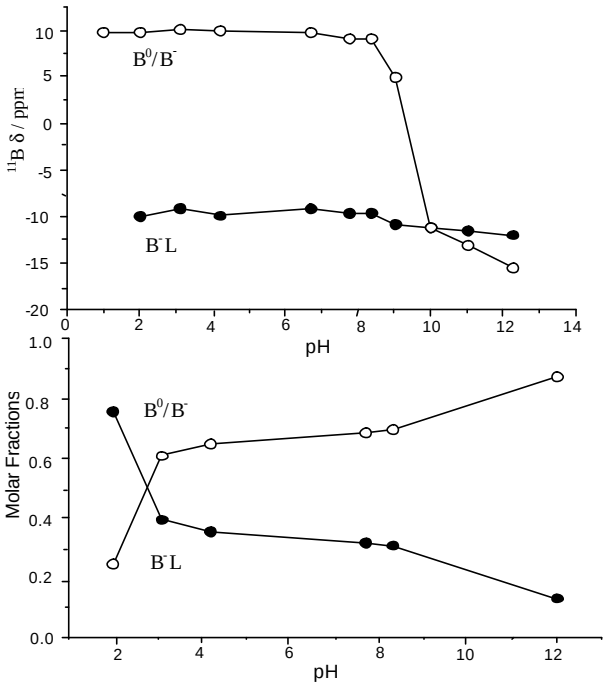

Figure 2S. pH dependence of the ^{11}B NMR shifts of a mixture of Neu5Ac and PBA (1:1, 0.6 M) and relative molar fractions.

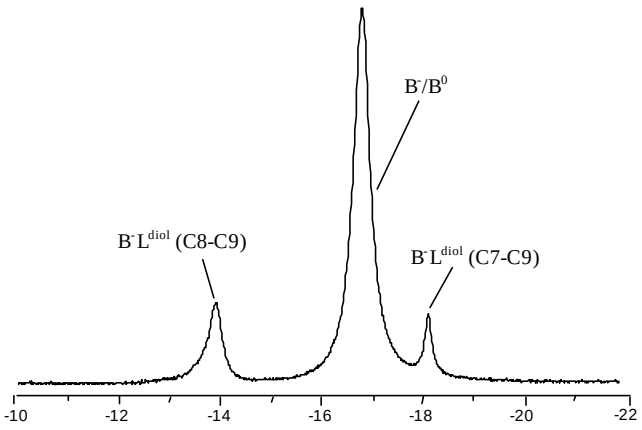

Figure 3S. ^{11}B NMR of a solution of 5 (74.8 mM) and H_3BO_3 (0.22 M) at pH 11.

Table 1S. Atomic coordinates (Å) Neu5Ac-Borate C8-C9 5-membered complex.

Atom	Coordinates (Å)			Atom	Coordinates (Å)		
	x	y	z		x	y	z
1 – O	-0.4029	1.9061	8.2358	24 – H	1.3596	-1.8241	9.0685
2 – O	-2.2531	-1.2260	8.0230	25 – H	2.6610	0.3323	5.2376
3 – O	-0.8374	0.8256	4.0116	26 – H	2.5223	0.7628	6.0928
4 – O	-0.1014	-0.9766	7.7290	27 – H	-0.2171	1.6159	5.7803
5 – O	1.8469	-2.3126	8.3935	28 – H	0.3554	-1.4011	5.1878
6 – O	4.0448	0.0310	6.6806	29 – H	0.2307	0.6011	7.4275
7 – O	5.6808	-1.4483	7.5435	30 – H	2.4451	-2.0408	6.4880
8 – O	-2.2999	1.2748	9.2226	31 – H	3.1741	0.1853	8.5344
9 – O	1.1239	-1.0336	2.8088	32 – H	4.8399	-1.2146	9.4062
10 – N	1.8632	-0.0151	4.7366	33 – H	0.1587	-0.7602	10.0644
11 – C	-1.3386	1.0827	3.4284	34 – H	0.2144	-0.5211	3.4797
12 – C	-1.3215	-0.2369	7.5927	35 – H	-2.0182	-0.9188	5.6408
13 – C	-1.6761	0.0318	6.1248	36 – H	4.2050	-2.6037	8.4088
14 – C	-0.4826	0.6006	5.3660	37 – H	-1.1433	-2.1861	9.5078
15 – C	0.7113	-0.3795	5.5236	38 – H	-2.9726	-2.3268	9.5417
16 – C	1.0266	-0.4406	7.0433	39 – H	3.4331	-0.7214	1.8359
17 – C	2.2003	-1.3898	7.3727	40 – H	3.4925	-0.9152	2.6268
18 – C	3.4647	-0.6058	7.7905	41 – B	5.3875	-0.5827	6.3627
19 – C	4.5501	-1.5374	8.3713	42 – O	5.3077	-1.3493	5.1818
20 – C	-2.1076	-1.6362	9.3722	43 – O	6.3457	0.4320	6.2159
21 – C	2.0388	-0.4542	3.4498	44 – H	4.7546	-2.0777	0.4594
22 – C	3.3788	-0.1800	2.8089	45 – H	6.2351	0.9183	7.0312
23 – H	-0.7031	-0.0043	3.5338				

Table 2S. Atomic coordinates (Å) Neu5Ac-Borate C7-C9 6-membered complex.

Atom	Coordinates (Å)			Atom	Coordinates (Å)		
	x	y	z		x	y	z
1 – O	-	188.8104	-	24 – H	-	189.1843	-
2 – O	-	188.1465	-	25 – H	-	187.9370	-
3 – O	-	188.7012	-	26 – H	-	188.2400	-
4 – O	-	190.0609	-	27 – H	-	187.8427	-
5 – O	-	189.0160	-	28 – H	-	189.3485	-
6 – O	-	190.1830	-	29 – H	-	187.7325	-
7 – O	-	188.3080	-	30 – H	-	190.3486	-
8 – O	-	187.0436	-	31 – H	-	191.5800	-
9 – O	-	190.6344	-	32 – H	-	192.8700	-
10 –	-	187.7880	-	33 – H	-	190.4160	-
11 –	-	189.3310	-	34 – H	-	191.6010	-
12 –	-	188.1005	-	35 – H	-	193.6713	-
13 –	-	191.1510	-	36 – H	-	192.7340	-
14 –	-	187.1079	-	37 – H	-	193.2214	-
15 –	-	188.3442	-	38 – H	-	191.7502	-
16 –	-	188.7940	-	39 – H	-	192.1900	-
17 –	-	187.1270	-	40 – H	-	191.4728	-
18 –	-	190.2190	-	41 – B	-	191.5161	-
19 –	-	189.5975	-	42 – O	-	191.5700	-
20 –	-	187.9190	-	43 – O	-	192.4248	-
21 –	-	189.1946	-	44 – H	-	189.4278	-
22 –	-	189.0710	-	45 – H	-	191.6134	-
23 –	-	189.1230	-				

Table S3. Atomic coordinates (Å) Neu5Ac-Borate C7-C8 6-membered complex.

Atom	Coordinates (Å)			Atom	Coordinates (Å)		
	x	y	z		x	y	z
1 – O	0.8953	2.4973	7.6847	24 – H	3.7952	-2.3990	2.5322
2 – O	2.1285	-0.4587	8.4417	25 – H	-1.4932	0.7806	3.9651
3 – O	-1.9738	-1.6446	6.3962	26 – H	-0.5515	-1.0163	8.5742
4 – O	1.7283	0.2096	6.3936	27 – H	-1.5636	0.3166	6.6892
5 – O	1.0514	0.7253	2.8922	28 – H	0.2269	-1.5154	4.9492
6 – O	3.4224	0.0764	2.5531	29 – H	0.3909	1.4982	5.5149
7 – O	3.7401	-2.4739	3.4697	30 – H	2.2386	1.7558	4.1600
8 – O	-0.1474	1.4478	9.3896	31 – H	3.7988	-0.0519	4.5442
9 – O	-1.4008	-2.3103	3.3037	32 – H	2.3907	-2.0839	4.9121
10 – N	-1.1459	-0.1752	4.0726	33 – H	3.6277	0.8361	7.8018
11 – C	0.6046	1.4271	8.2188	34 – H	-2.0458	0.1247	10.4944
12 – C	1.0977	0.1046	1.6529	35 – H	0.4246	-1.9524	7.4031
13 – C	-0.0211	-0.9470	7.5950	36 – H	1.7786	-2.0167	3.1899
14 – C	-1.0081	-0.6264	6.4725	37 – H	3.9718	-0.2010	9.2487
15 – C	-0.2388	-0.5260	5.1499	38 – H	2.8543	1.2087	9.4355
16 – C	0.8818	0.5191	5.3038	39 – H	-2.9530	-1.4363	1.4884
17 – C	1.7970	0.7305	4.0838	40 – H	-3.4628	-0.1091	2.6017
18 – C	2.9540	-0.2508	3.8418	41 – B	2.1402	0.5233	1.8172
19 – C	2.6127	-1.7428	3.8757	42 – O	1.6892	-0.5538	0.8138
20 – C	3.1966	0.4120	8.7373	43 – O	2.4078	1.8461	1.0750
21 – C	-1.6522	-1.1317	3.2150	44 – H	2.3840	-0.5808	0.1786
22 – C	-2.5829	-0.6096	2.1370	45 – H	2.6724	2.4437	1.7534
23 – H	-1.7584	-2.2221	5.6842				

Table S4. Atomic coordinates (Å)Neu5Ac-PBA (Boron in *R*-configuration) C8-C9
6-membered complex.

Atom	Coordinates (Å)			Atom	Coordinates (Å)		
	x	y	z		x	y	z
1 – O	-0.5181	2.8717	8.2625	28 – H	0.3093	-0.9414	5.8971
2 – O	-2.7741	0.0260	7.9593	29 – H	1.0103	1.2535	8.0141
3 – O	-0.1679	1.2398	4.2111	30 – H	1.9725	-1.6225	7.7342
4 – O	-0.6013	-0.0645	8.1760	31 – H	2.4951	0.7235	0.7174
5 – O	0.9014	-1.5478	9.4388	32 – H	3.7971	-0.7620	10.9900
6 – O	3.7195	0.3537	0.1109	33 – H	-	-0.7330	9.3678
7 – O	4.9360	1.2634	9.3498	34 – H	4.5542	-0.7891	0.9162
8 – O	-2.6703	2.6675	0.8106	35 – H	-	-0.0577	5.6877
9 – O	1.5928	-1.0060	0.7029	36 – H	3.1834	-2.1513	9.9775
10 – N	2.1053	0.1074	5.6523	37 – H	-	0.7923	0.8833
11 – C	-1.6001	2.2257	8.3096	38 – H	-	-0.8108	9.7854
12 – C	-1.6185	0.8046	7.6610	39 – H	4.0577	-1.1016	3.1834
13 – C	-1.5838	0.8960	6.1302	40 – H	4.1940	0.6030	3.8021
14 – C	-0.1707	1.1665	5.6263	41 – B	5.0135	-0.4175	8.1221
15 – C	0.7647	0.0564	6.1799	42 – O	4.9750	-1.2941	6.9943
16 – C	0.7240	0.1998	7.7261	43 – C	6.2792	0.5188	8.1069
17 – C	1.6215	0.8272	8.4488	44 – H	4.2332	-1.8626	0.1935
18 – C	2.8469	-0.1450	9.0970	45 – C	6.1534	1.9112	0.1914
19 – C	3.6662	-1.1398	9.9417	46 – C	7.2821	2.7297	0.1892
20 – C	-3.0143	-0.1816	9.3400	47 – C	8.5563	2.1683	0.1028
21 – C	0.4465	-0.4774	4.4617	48 – C	8.6937	0.7831	8.0167
22 – C	3.9051	-0.4416	4.0691	49 – C	7.5634	-0.0333	8.0178
23 – H	-0.1310	0.3345	3.8735	50 – H	5.1438	2.3469	8.2580
24 – H	0.3394	-0.9166	9.9056	51 – H	7.1693	3.8206	8.2554
25 – H	2.8337	0.4031	6.2767	52 – H	9.4449		
26 – H	-2.2602	1.7277	5.8103	53 – H	9.6952		
27 – H	0.1718	2.1824	5.9787	54 – H	7.6633		

Table S5. Atomic coordinates (Å) Neu5Ac-PBA C8-C9 (Boron in *S*-configuration) 5-membered complex.

Atom	Coordinates (Å)			Atom	Coordinates (Å)		
	x	y	z		x	y	z
1 – O	-0.4267	1.8561	8.4728	28 – H	-	-	5.1980
2 – O	-2.3244	-1.2495	8.3063	29 – H	1.0717	0.6090	7.4504
3 – O	-1.3256	1.0034	4.2722	30 – H	2.1272	-	6.2882
4 – O	-0.2158	-0.9929	7.7912	31 – H	3.1510	0.3884	7.8702
5 – O	1.8316	2.2626	8.2707	32 – H	4.6160	-	9.1565
6 – O	3.9300	0.3304	6.1011	33 – H	-	-	10.3492
7 – O	5.6228	-1.3424	0.4202	34 – H	3.6397	-	3.1649
8 – O	-2.2375	1.2072	9.6000	35 – H	-	-	5.9222
9 – O	0.5207	-0.7800	2.7842	36 – H	4.1294	-	8.3232
10 – N	1.4363	0.1542	4.6786	37 – H	-	-	9.6481
11 – C	-1.3558	1.0373	8.7146	38 – H	-	-	9.8314
12 – C	-1.4388	0.2436	7.8244	39 – H	2.7106	0.3938	1.5957
13 – C	-1.9445	0.0942	6.4161	40 – H	3.0112	1.0983	2.5932
14 – C	-0.8365	0.7116	5.5706	41 – B	5.3990	0.6754	6.1029
15 – C	0.3697	-0.2657	5.5548	42 – O	5.8140	-	4.8846
16 – C	0.8368	-0.4110	7.0280	43 – C	6.1128	0.5579	6.1202
17 – C	2.0393	-1.3716	7.1853	44 – H	5.7660	0.9892	6.8986
18 – C	3.3630	-0.5958	7.3653	45 – C	4.9002	-	4.2857
19 – C	4.4279	-1.3736	8.1607	46 – C	5.2842	-	3.2223
20 – C	-2.0473	-1.7091	9.6190	47 – C	6.5911	-	2.7382
21 – C	1.4994	-0.2497	3.3678	48 – C	7.5103	-	3.3237
22 – C	2.7950	0.0043	2.6338	49 – C	7.1233	-	4.3865
23 – H	-1.2423	0.1990	3.7420	50 – H	3.8694	-	0.6726
24 – H	1.4437	-1.7535	8.9932	51 – H	4.5556	-	2.7635
25 – H	2.2820	0.4598	5.1196	52 – H	6.8943	-	1.9014
26 – H	-2.7924	0.8181	6.5080	53 – H	8.5403	-	2.9438
27 – H	-0.5333	1.7063	6.0084	54 – H	7.8346	-	4.8499

Table S6. Atomic coordinates (Å) Neu5Ac-PBA C7-C8 (Boron in *R*-configuration) 5-membered complex.

Atom	Coordinates (Å)			Atom	Coordinates (Å)		
	x	y	z		x	y	z
1 – O	-0.0092	42.1984	8.0026	28 – H	-0.0516	-1.1800	4.9645
2 – O	1.2191	-1.1949	8.5520	29 – H	0.6622	1.6960	5.9227
3 – O	-2.5974	-0.4572	5.8715	30 – H	2.8945	1.5365	5.2261
4 – O	1.4972	-0.0587	6.6978	31 – H	4.0155	-0.3360	4.6521
5 – O	1.7886	1.6060	3.4952	32 – H	2.2132	-1.9473	5.3642
6 – O	3.2710	-0.0920	2.7571	33 – H	3.2410	-1.0939	8.0726
7 – O	3.2657	-2.7109	3.7955	34 – H	-0.8436	0.4722	1.0538
8 – O	0.8799	1.2463	9.8105	35 – H	-0.7179	-1.7613	7.2387
9 – O	-1.9997	-1.4617	3.2896	36 – H	1.4268	-1.7643	3.7054
10 – N	-0.7506	0.4161	3.7918	37 – H	2.7605	-1.7559	9.7153
11 – C	0.4993	1.2145	8.6084	38 – H	2.6840	0.0541	9.3933
12 – C	0.6121	-0.1318	7.8232	39 – H	-2.3548	-0.5508	0.9799
13 – C	-0.7768	-0.6600	7.4377	40 – H	-2.4262	1.1309	1.6672
14 – C	-1.3234	0.0611	6.2104	41 – B	2.4274	1.0375	2.2619
15 – C	-0.2788	-0.0761	5.0600	42 – O	1.3714	0.4753	1.4782
16 – C	0.9873	0.6660	5.5799	43 – C	3.2528	2.1119	1.4582
17 – C	2.1872	0.8762	4.6366	44 – H	1.1734	-0.3395	1.9379
18 – C	3.0169	-0.3217	4.1307	45 – C	4.2961	1.7201	0.6100
19 – C	2.3880	-1.7059	4.2831	46 – C	5.0207	2.6655	-
20 – C	2.5598	-0.9634	8.9500	47 – C	4.7128	4.0210	-
21 – C	-1.5125	-0.3538	2.9495	48 – C	2.9571	3.4767	1.5692
22 – C	-1.8003	0.2115	1.5757	49 – C	3.6796	4.4237	0.8451
23 – H	-2.4559	-1.2834	5.3899	50 – H	4.5396	0.6503	0.5326
24 – H	3.6160	-2.3784	2.9585	51 – H	5.8375	2.3447	-
25 – H	-0.2156	1.1641	3.3862	52 – H	5.2819	4.7664	-
26 – H	-1.4688	-0.4991	8.3016	53 – H	0.1489	3.7867	2.2495
27 – H	-1.5019	1.1482	6.4563	54 – H	3.4385	5.4913	0.9421

Table S7. Atomic coordinates (Å) Neu5Ac-PBA C7-C8 (Boron in *S*-configuration) 5-membered complex.

Atom	Coordinates (Å)			Atom	Coordinates (Å)		
	x	y	z		x	y	z
1 – O	-0.4951	2.6013	7.0516	28 – H	0.6739	-1.6702	6.0303
2 – O	1.7101	0.4680	9.0257	29 – H	0.4811	1.3742	5.3991
3 – O	-2.0025	-1.3443	6.7399	30 – H	2.7079	1.4983	4.6620
4 – O	1.7448	0.5341	6.8411	31 – H	4.2814	-0.0815	5.1419
5 – O	1.7312	0.3906	3.2195	32 – H	2.9427	-1.7794	6.3516
6 – O	3.8020	-0.7658	3.2644	33 – H	3.6578	0.7191	9.5233
7 – O	4.1926	-2.7820	5.0953	34 – H	-0.1938	-2.7146	1.9762
8 – O	0.7319	3.0450	8.8595	35 – H	0.0967	-1.1986	8.3683
9 – O	-0.9754	-3.2697	4.8954	36 – H	2.1949	-2.3540	4.7665
10 – N	-0.4028	-1.1112	4.3141	37 – H	2.5095	2.0400	10.0985
11 – C	0.3309	2.2722	7.9474	38 – H	3.0182	1.9758	8.3455
12 – C	0.8564	0.8006	7.9372	39 – H	-1.6430	-3.6825	2.5120
13 – C	-0.2933	-0.2126	8.0060	40 – H	-1.8189	-1.9115	2.1387
14 – C	-0.9635	-0.3851	6.6470	41 – B	2.8062	-0.1561	2.3184
15 – C	0.1315	-0.7690	5.6100	42 – O	2.2476	-1.1834	1.2627
16 – C	1.1038	0.4430	5.5693	43 – C	3.4506	0.9485	1.6918
17 – C	2.2409	0.4720	4.5361	44 – H	1.6963	-0.7319	0.0563
18 – C	3.4052	-0.5384	4.6038	45 – C	3.7438	1.4719	2.4352
19 – C	3.0976	-1.8900	5.2472	46 – C	1.2181	-1.6345	-0.8923
20 – C	2.7845	1.3661	9.2494	47 – C	1.2849	-3.0068	-0.6496
21 – C	-0.8209	-2.3842	4.0172	48 – C	1.8338	-3.4687	0.5466
22 – C	-1.1437	-2.6869	2.5714	49 – C	2.3113	-2.5632	1.4939
23 – H	-1.5951	-2.2195	6.6908	50 – H	1.6588	0.3518	-0.1304
24 – H	4.5142	-2.6644	4.1906	51 – H	0.7881	-1.2674	-1.8343
25 – H	-0.1210	-0.5163	3.5589	52 – H	0.9080	-3.7186	-1.3954
26 – H	-1.0467	0.1574	8.7461	53 – H	1.8887	-4.5485	0.7422
27 – H	-1.4730	0.5776	6.3515	54 – H	2.7522	-2.9189	2.4395