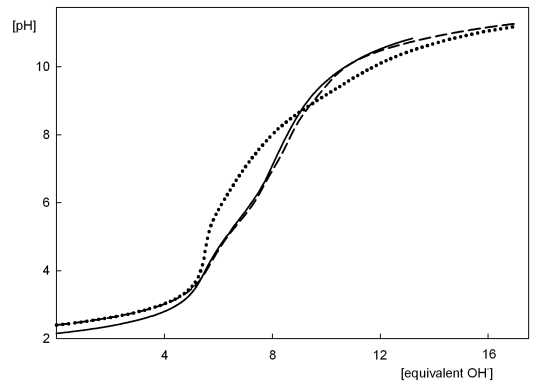
Supplement

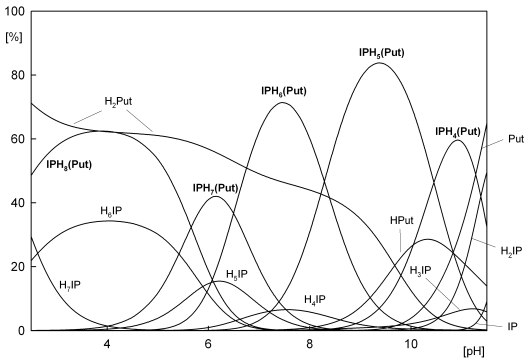


Supplemental Figure 1 Experimental and simulated titration curves for IP/Spm system. c_{IP}=c_{Spm}=0.001M

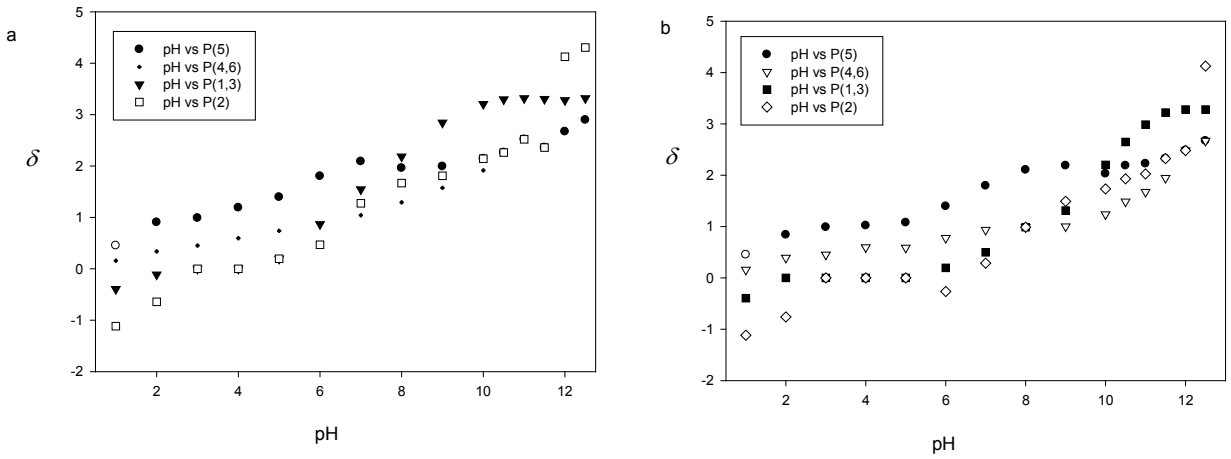
——— experimental titration curve for IP/Spm system

····· simulated titration curve for IP/Spm system; adduct formation was not taken into account

– – – – simulated titration curve for IP/Spm system; adduct formation was taken into account



Supplemental Figure 2 Distribution diagram for IP/Put system. Percentage refers to total IP; c_{IP}=0.001M, c_{Put}=0.001M

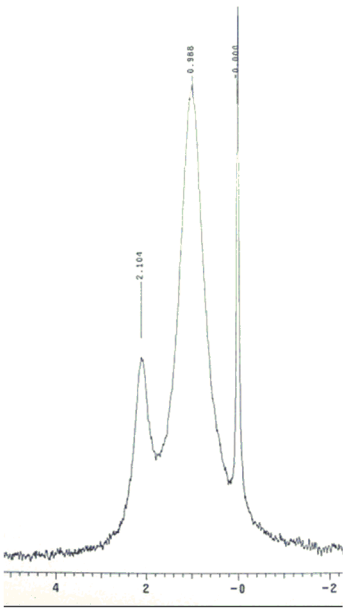


Supplemental Figure 3 Plot δ in ^{31}P-NMR vs. pH for a) H_n(IP) and (IP)H_n(Spm) systems

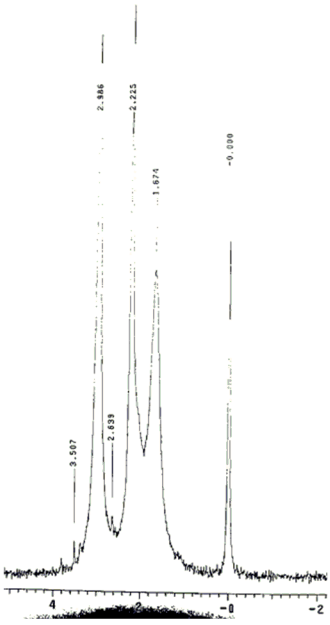
Supplemental Figure 4 ^{31}P NMR spectra for IP and IP/Spm systems

IP

pH 8

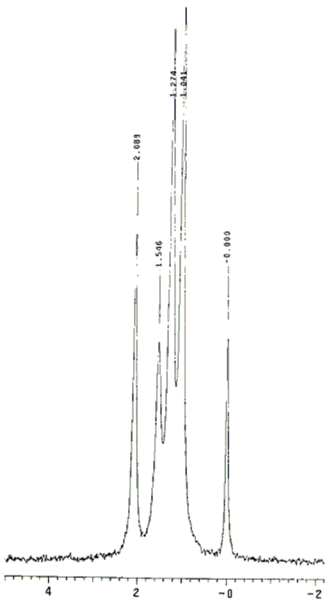


pH 11

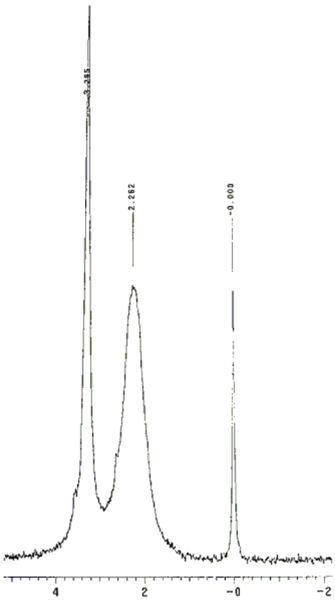


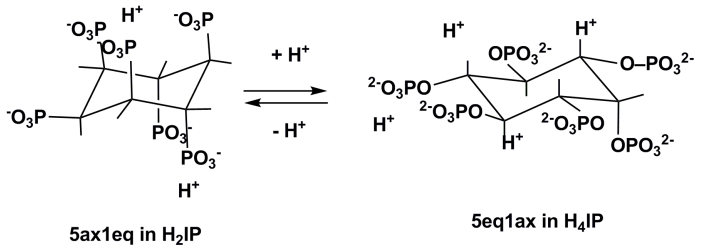
IP/Spm

pH 8



pH 11





5ax1eq in H_2IP

5eq1ax in H_4IP

Supplemental Figure 5 Possible preffered conformations of 5ax1eq in H_2IP and 5eq1ax in H_4IP

Supplemental Table 1 ^{31}NMR shifts for IP and IP/Spm systems

IP system

pH	P(5)	P(4,6)	P(1,3)	P(2)
1	0.596	0.287	-0.256	-0.95
3	--	0.437	0	0
4	--	0.596	0	0
5	1.395	0.739	0.196	0.196
6	1.802	0.867	0.468	0.468
7	2.089	1.041	1.546	1.274
8	1.961	1.292	2.184	1.667
9	1.991	1.576	2.843	1.81
10	2.142	1.915	3.205	2.142
10.5	2.262	2.262	3.295	2.262
11	2.519	2.519	3.318	2.519
11.5	2.36	2.36	3.303	2.36
12	2.67	2.67	3.28	4.125
12.5	2.896	2.896	3.318	4.306

IP/Spm

pH	P(5)spm	P(4,6)spm	P(1,3)spm	P(2)spm
1	0.452	0.158	-0.395	-1.116
3	0.988	0.452	0	0
4	--	--	0	0
5	1.078	0.588	0	0
6	1.395	0.777	0.196	-0.264
7	1.795	0.935	0.498	0.287
8	2.104	0.988	0.988	0.988
9	2.187	1.003	1.312	1.493
10	2.029	1.237	2.202	1.734
10.5	2.187	1.486	2.647	1.931
11	2.225	1.674	2.986	2.025
11.5	2.323	1.946	3.22	2.323
12	2.481	2.481	3.28	2.481
12.5	2.67	2.67	3.28	4.125

Difference(IP-IP/Spm)

pH	P(5)	P(4,6)	P(1,3)	P(2)
1	0.144	0.158	0.139	0.166
3		0.452	0	0
4		--	0	0
5	0.317	0.588	0.196	0.196
6	0.407	0.777	0.272	0.732
7	0.294	0.935	1.048	0.987
8	-0.143	0.988	1.196	0.679
9	-0.196	1.003	1.531	0.317
10	0.113	1.237	1.003	0.408
10.5	0.075	1.486	0.648	0.331
11	0.294	1.674	0.332	0.494
11.5	0.037	1.946	0.083	0.037
12	0.189	2.481	0	1.644
12.5	0.226	2.67	0.038	0.181

Supplemental Table 2 IP and IP/Spm experimental condition for ^{31}P NMR Measurment

number	V_{sample} [cm^3]	$V_{[(Et)4N]OH}$ [cm^3]	mol of IP	mol of $[(Et)_4N]OH$	pH
IP					
1.	21	---	0.00066990	---	0.86
2.	20.1	0.930	0.00064119	0.0022599	1.98
3.	19.1	1.251	0.00060929	0.0030399	2.99
4.	18.1	1.414	0.00057739	0.0034360	4.33
5.	17.1	1.468	0.00054549	0.0035672	4.99
6.	16.1	1.600	0.00051359	0.0038880	5.87
7.	15.1	1.780	0.00048169	0.0043254	6.93
8.	14.1	1.920	0.00044979	0.0046656	7.85
9.	13.1	2.030	0.00041789	0.0049329	8.92
10.	12.1	2.140	0.00038599	0.0052002	9.82
11.	11.1	2.235	0.00035409	0.0054310	10.47
12.	10.1	2.325	0.00032219	0.0056498	10.96
13.	9.1	2.445	0.00029029	0.0059414	11.51
14.	8.1	2.545	0.00025839	0.0061844	11.98
15.	7.1	2.645	0.00022649	0.0064274	12.50
IP/Spm					
16.	21	---	0.0006699	---	0.96
17.	20	0.771	0.0006380	0.0018735	1.99
18.	19	0.970	0.0006061	0.0023571	2.97
19.	18	1.115	0.0005742	0.0027094	4.29
20.	17	1.220	0.0005423	0.0029646	4.97
21.	16	1.375	0.0005104	0.0033412	5.86
22.	15	1.526	0.0004785	0.0037082	6.92
23.	14	1.630	0.0004466	0.0039609	7.86
24.	13	1.770	0.0004147	0.0043011	8.94
25.	12	1.920	0.0003828	0.0046656	9.86
26.	11	2.070	0.0003509	0.0050301	10.51
27.	10	2.181	0.0003190	0.0052998	10.95
28.	9	2.330	0.0002871	0.0056619	11.47
29.	8	2.480	0.0002552	0.0060264	11.99
30.	7	2.615	0.0002233	0.0063544	12.49