Supporting Information:

General Methods: Deuterium oxide (Merck) and methanol-d_4 (Merck) were purchased each in 99.8% purity. 2-hexanone (Aldrich) and lithiumbromide (Merk) were also purchased each in 99% purity.

17,17,40,40-Tetramethyl-1,10,24,33-tetraoxy[2](2,6)pyridino[2.1]paracyclo[2](2,6)-pyridino[2.1]paracyclophane-12,20,35,43-tetraphosphonic acid monoethylester tetra lithium salt. 146.7 mg (0.1215 mmol) of the macrocycle, 46.3 mg (4.1 eq.) of lithiumbromide were dissolved in 7 ml of dry 2-hexanone under argon atmosphere and heated for 120 hours at 100°C. The residue was filtrated and washed with 2 hexanone. The salt was purified via dialysis; afterwards it contained only minute amounts of lithiumbromide. Yield: 116 mg (85%). ^{1}H-NMR (500 MHz, CD_3OD): δ = 1.13 (t, 12 H, J = 7.3 Hz, $CH_3$$CH_2$O), 1.64 (s, 12 H, CH_3C), 3.81 (q, 8 H, J = 7.0 Hz, $CH_3$$CH_2$O), 5.26 (s, 8 H, CH_2O), 6.76 und 6.90 (m, 2 x 4 $H_{arom.}$), 7.69 (d, 4 H_{py}, J = 6.9 Hz), 7.76 (t, 2 H_{py}, J = 6.9 Hz), 7.86 (m, 4 $H_{arom.}$). ^{13}C-NMR (125 MHz, CD_3OD) δ = 17.44 (s), 31.87 (s), 39.00 (s), 43.37 (s), 61.74 (d, 5.0 Hz), 113.75 (d, 8.8 Hz), 122.36 (s), 123.92 (s), 125.31 (s), 129.36 (d, 82.3 Hz), 132.39 (s), 133.58 (d, 6.8 Hz), 139.68 (s), 144.36 (d, 12.5 Hz), 159.01 (d, 42,3 Hz). ^{31}P-NMR (200 MHz, CD_3OD) δ = 12.85. Anal. Cacld for $C_{52}H_{58}N_2O_{16}P_4Li_4$: C 55.83; H 5.23; N 2.50. Found: C 54.71; H 5.45; N 2.08. MS (FAB, glycine matrix, Xe): *m/z* 1125 (M + Li^+, 55%).

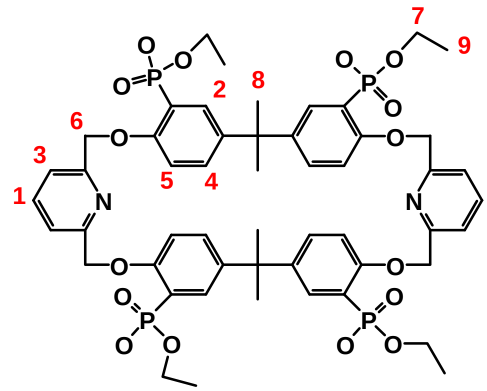
^{1}H NMR Titrations.

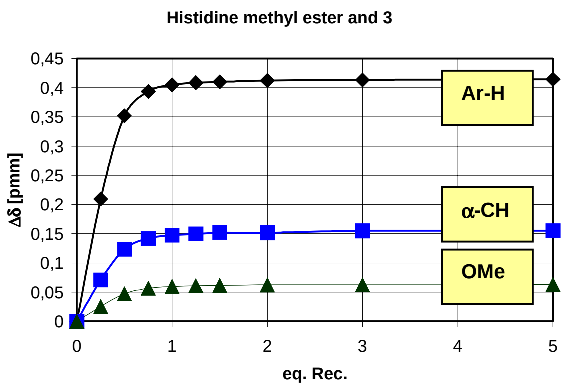
Ten NMR tubes were filled each with 0.8 mL of a solution of the host compound (c_{guest} = 0.5–4 mM) in a deuterated solvent (methanol-d_4, or D_2O). The guest compound (1.525 equiv corresponding to the guest) was dissolved in 0.61 mL of the same solvent, and the resulting solution was added with increasing volumes from 0 to 5 equiv. to the guest solution in ten NMR tubes.

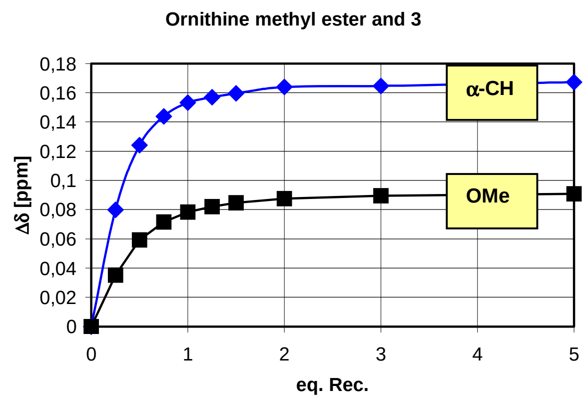
Volume and concentration changes were taken into account during analysis. The association constants were calculated by non-linear regression methods.

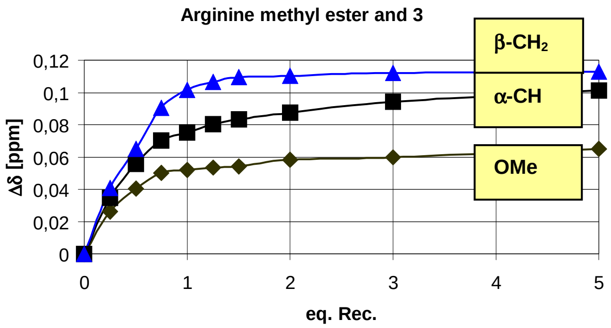
Job plots. Equimolar solutions (10 mmol/10 mL, approx. 10 µM) of dication and tetraphosphonate were prepared and mixed in various amounts. ^{1}H NMR spectra of the mixtures were recorded, and the chemical shifts were analysed by Job's method modified for NMR results.

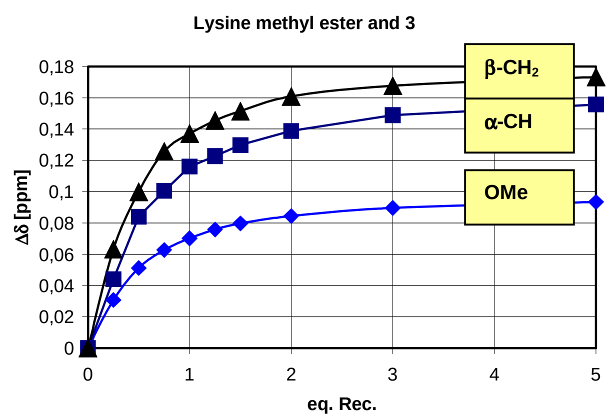
1. NMR titrations in methanol



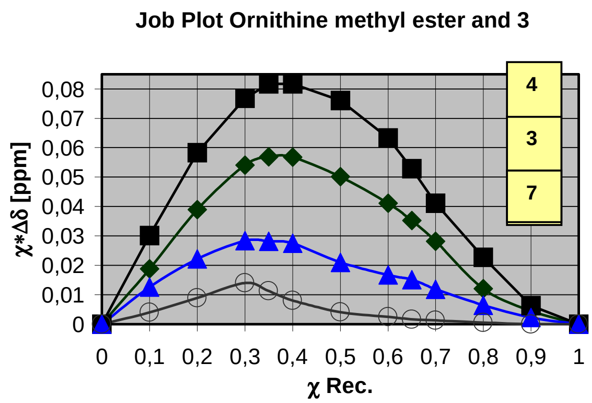


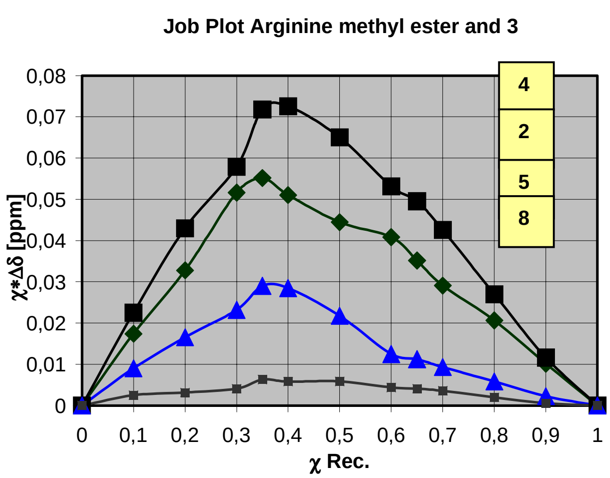




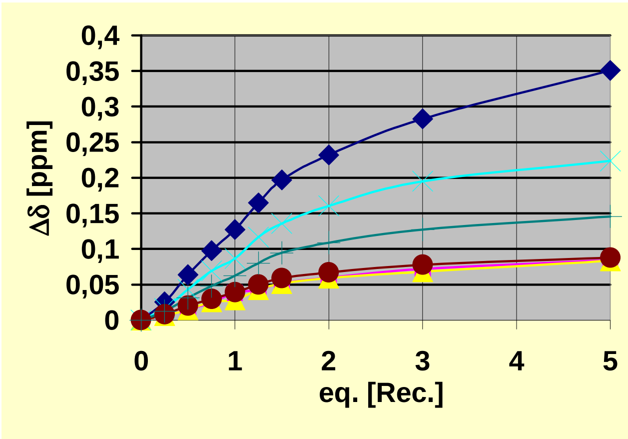


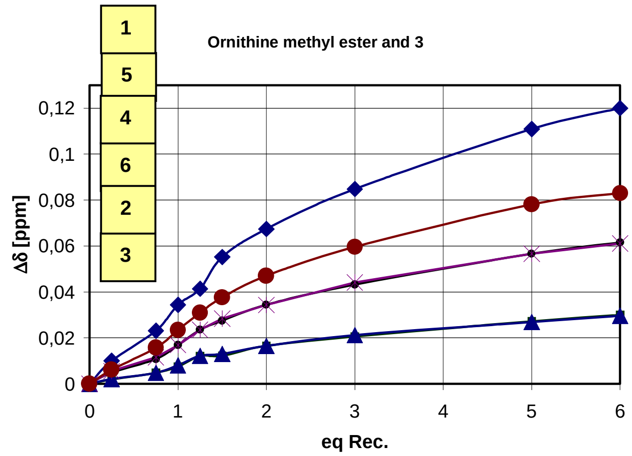
2. Job-Plots in methanol

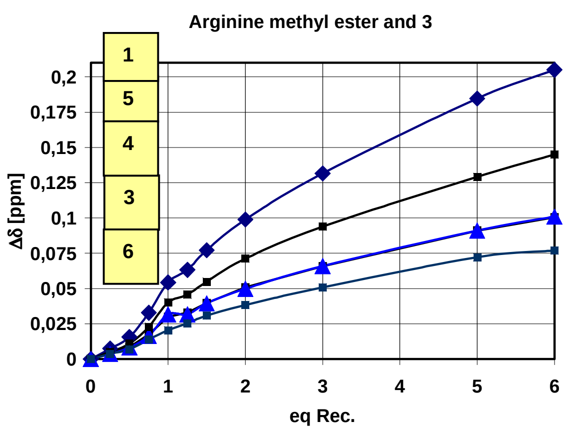


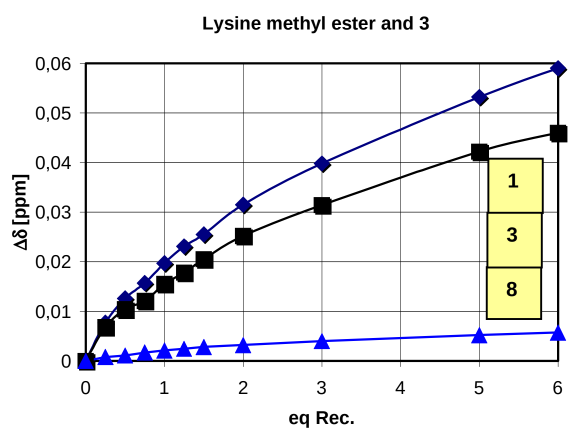


3. NMR titrations in water









4. Tables

Table 1: Histidine in methanol

Eq Guest	Δδ H^1	Δδ H^2	Δδ CH^3		K_a /Error (averaged)
0,25	**0,2093**	**0,0709**	**0,0255**		
0,5	**0,3518**	**0,1235**	**0,0472**		
0,75	**0,3934**	**0,1421**	**0,0567**		
1	**0,4047**	**0,1475**	**0,0595**		
1,25	**0,4084**	**0,1496**	**0,061**		
1,5	**0,4097**	**0,1518**	**0,0614**		
2	**0,4122**	**0,1516**	**0,0624**		
3	**0,4132**	**0,155**	**0,0626**		**K_a =29000**
5	**0,4141**	**0,1551**	**0,0629**		**Error:+/-11%**

Table 2: Ornithine in methanol:

Eq Guest	Δδ H^1	Δδ H^2		K_a /Error (averaged)
0,25	**0,0799**	**0,0351**		
0,5	**0,1242**	**0,0592**		
0,75	**0,1439**	**0,0715**		
1	**0,1533**	**0,0783**		
1,25	**0,1569**	**0,0821**		
1,5	**0,1596**	**0,0846**		
2	**0,1639**	**0,0875**		
3	**0,1647**	**0,0895**		**K_a =18000**
5	**0,1673**	**0,0908**		**Error:+/-30%**

Table 3: Arginine in methanol

Eq Guest	Δδ H^1	Δδ H^2	Δδ H^3		K_a /Error (averaged)
0,25	**0,02606**	**0,0347**	**0,04076**		
0,5	**0,0405**	**0,0558**	**0,065**		
0,75	**0,05018**	**0,0704**	**0,0905**		
1	**0,052**	**0,0751**	**0,1018**		
1,25	**0,0533**	**0,0804**	**0,1065**		
1,5	**0,0541**	**0,0832**	**0,1094**		
2	**0,0583**	**0,0874**	**0,1103**		
3	**0,06**	**0,0942**	**0,1122**		**K_a = 30000**
5	**0,065**	**0,1012**	**0,1129**		**Error: +/-15%**

Table 4: Lysine in methanol

Eq Guest	Δδ H^1	Δδ H^2	Δδ H^3		K_a /Error (averaged)
0,25	**0,0307**	**0,044**	**0,0632**		
0,5	**0,0512**	**0,084**	**0,0999**		
0,75	**0,0627**	**0,1005**	**0,1258**		
1	**0,0701**	**0,116**	**0,1371**		
1,25	**0,0758**	**0,1227**	**0,1455**		
1,5	**0,0797**	**0,1298**	**0,1515**		
2	**0,0844**	**0,1388**	**0,1609**		
3	**0,0896**	**0,1489**	**0,1677**		**K_a = 21000**
5	**0,0934**	**0,1557**	**0,1733**		**Error +/-35%**

Table 5: Histidine in water

Eq Guest	Δδ H^1	Δδ H^2	Δδ CH^3	Δδ H^4	Δδ H^5	Δδ H^6	Δδ H^2	K_a/ Error (averaged)
0	0	0	0	0	0	0	0	
0,25	0,0255	0,006	0,0063	0,0161	0,0275	0,0081	0,0126	
0,5	0,0637	0,0148	0,0145	0,0432	0,0489	0,0204	0,0312	
0,75	0,0977	0,0249	0,0258	0,0693	0,0489	0,0296	0,0479	
1	0,1274	0,0384	0,0283	0,0864	0,0773	0,039	0,0624	
1,25	0,1649	0,0428	0,0428	0,1166	0,0814	0,0501	0,0801	
1,5	0,197	0,052	0,0514	0,1359	0,0971	0,0589	0,0946	
2	0,232	0,0595	0,0592	0,1604	0,1126	0,0671	0,1087	
3	0,2827	0,0718	0,0681	0,1951	0,1349	0,0778	0,1273	K_a = 650 M^{-1}
5	0,3508	0,0844	0,0835	0,2235	0,162	0,0879	0,1456	Error = +/- 18%

Table 6: Ornithine in water

Eq Guest	Δδ H^1	Δδ H^2	Δδ CH^3	Δδ H^4	Δδ H^5	Δδ H^6		K_a/ Error (averaged)
0,25	0,01	0,0019	0,0021	0,0049	0,0055	0,0061		
0,75	0,0231	0,0048	0,0048	0,0108	0,0115	0,0157		
1	0,0344	0,0075	0,0081	0,0169	0,0169	0,0234		
1,25	0,0414	0,0121	0,0122	0,0235	0,0235	0,0309		
1,5	0,0552	0,0122	0,013	0,0275	0,0284	0,0376		
2	0,0674	0,0165	0,0165	0,0344	0,0343	0,047		
3	0,0848	0,0206	0,0212	0,0432	0,0441	0,0596		
5	0,1109	0,0272	0,0269	0,0566	0,0566	0,0781		K_a = 450
6	0,12	0,03	0,0296	0,0615	0,0611	0,083		Error = +/- 33%

Table 7: Arginine in water

Eq Gast	Δδ H^1	Δδ H^2	Δδ CH^3	Δδ H^4	Δδ H^5		K_a/ Error (averaged)
0,25	0,0074	0,004	0,0036	0,0051	0,0037		
0,5	0,0156	0,0084	0,0082	0,0109	0,007		
0,75	0,0328	0,0175	0,0164	0,0229	0,0139		
1	0,0543	0,03	0,0317	0,0401	0,0204		
1,25	0,0632	0,0328	0,0317	0,0457	0,0254		
1,5	0,0772	0,0396	0,0395	0,0549	0,0308		
2	0,0989	0,0508	0,0498	0,0712	0,0383		
3	0,1316	0,0658	0,0659	0,0939	0,0508		
5	0,1847	0,0911	0,0911	0,1292	0,0722		K_a = 350
6	0,205004	0,10054	0,101	0,145	0,077		Error: +/-38%

Table 8: Lysine in water

Eq Guest	$\Delta\delta$ H^1	$\Delta\delta$ H^2	$\Delta\delta$ CH^3		K_a/ Error (averaged)
0,25	**0,0077**	**0,0068**	**8,00000E**		
0,5	**0,0126**	**0,0104**	**0,0011**		
0,75	**0,0157**	**0,0121**	**0,0017**		
1	**0,0197**	**0,0155**	**0,0021**		
1,25	**0,0231**	**0,0178**	**0,00245**		
1,5	**0,0255**	**0,0205**	**0,0028**		
2	**0,0315**	**0,0252**	**0,0032**		
3	**0,0398**	**0,0314**	**0,004**		
5	**0,0532**	**0,0422**	**0,0052**		
6	**0,059**	**0,04601**	**0,005705**		
K_a	**1061,388**	**1135,354**	**1411,877**		
$\Delta\delta_{sat}$	**0,1052**	**0,080483**	**0,009067**		**K_a = 1200**
Error [%]	**+/-23,44**	**+/-26,05**	**+/-25,93**		**Error +/-25%**

5. Job-Plots in water