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Table S1. Bond Lengths (Å) and Mulliken Atomic Charges for 9-13

	13	**13(N-2)$^+$**	**13(N-4)$^+$**	**9**	**12**	**10**	**11**
Bond lengths							
O(1)-N(2)	1.412	1.367	1.421	1.433	1.386	1.440	1.426
N(2)-C(3)	1.309	1.323	1.296	1.309	1.332	1.289	1.309
C(3)-N(4)	1.380	1.350	1.390	1.374	1.327	1.391	1.393
N(4)-C(5)	1.300	1.307	1.324	1.313	1.338	1.348	1.283
C(5)-O(1)	1.341	1.349	1.299	1.344	1.363	1.084	1.321
C(5)-N(exocyclic)				1.367	1.319	1.321	1.463
Charge on							
O(1)	-0.035	-0.098	-0.074	-0.234	-0.170	-0.163	-0.171
N(2)	+0.001	-0.084 (+0.385)[a]	+0.049	-0.082	-0.129 (+0.324)[a]	+0.030	+0.019
N(4)	-0.033	-0.136	-0.297 (+0.161)[a]	-0.314	-0.221	-0.399 (+0.035)[a]	-0.218
C(5)	-0.045	+0.169	+0.149	+0.414	+0.493	+0.551	+0.413
N(exocyclic)				-0.697 (+0.062)[a]	-0.646 (+0.240)[a]	-0.669 (+0.221)[a]	-0.749 (+0.705)[a]

[a]Group charge.

Table S2. Calculated or Measured Apparent Kinetic Constants (at 293.15 K) and Activation Parameters for the Rearrangement of 3a into 6a at Various pS^+ in 1:1 (v:v) Dioxane/Water

pS^{+a}	0.10	0.18	0.25	0.29	0.33	0.40	0.49	0.58
$10^5(k_{A,R})_{\mathbf{3a}}{}^b$	10.1	9.44	8.91	8.51	8.17	7.50	6.65	5.79
$\Delta H^{\#c}$	86	85	85	85	85	85	85	86
$\Delta S^{\#d}$	-29	-31	-31	-33	-36	-34	-35	-33
pS^{+a}	0.71	0.80	0.89	1.11	1.21[e]	1.80[e]	2.30[e]	2.80[e]
$10^6(k_{A,R})_{\mathbf{3a}}{}^b$	48.5	42.3	36.4	23.3	19.5	5.58	2.04	0.867
$\Delta H^{\#c}$	86	85	85	85	84	84	86	89
$\Delta S^{\#d}$	-35	-38	-40	-42	-49	-58	-59	-57
pS^{+e}	3.60	4.35	4.98	6.20	6.95	7.48	8.50	9.16[f]
$10^6(k_{A,R})_{\mathbf{3a}}{}^b$	0.600	0.604	0.604	0.605	0.693	0.713	1.31	2.47
$\Delta H^{\#c}$	95	95	96	96	96	97	92	92
$\Delta S^{\#d}$	-38	-38	-37	-37	-37	-33	-43	-40
pS^{+f}	9.60	9.88	10.19	10.45	10.79	11.10	11.45	11.70
$10^5(k_{A,R})_{\mathbf{3a}}{}^b$	0.658	1.25	2.12	4.05	7.53	15.8	32.7	55.3
$\Delta H^{\#c}$	89	88	92	88	92	89	88	88
$\Delta S^{\#d}$	-39	-37	-22	-28	-11	-14	-12	-7
pS^{+f}	11.81	11.97	12.10	12.25	12.35	12.66	12.81	12.95
$10^3(k_{A,R})_{\mathbf{3a}}{}^g$	0.676[b]	0.948[b]	1.28[b]	1.81	1.98	4.48	6.10	8.49
$\Delta H^{\#c}$	84	87	80					
$\Delta S^{\#d}$	-18	-5	-28					
pS^{+f}	13.27	13.47	13,65	13.86	14.01	14.25	14.48	14.65
$10^3(k_{A,R})_{\mathbf{3a}}{}^g$	18.0	28.0	40.0	65.0	97.9	150	260	350
pS^{+f}	14.82	14.90						
$10^3(k_{A,R})_{\mathbf{3a}}{}^g$	500	610						

[a] NaCl/HCl buffer. [b] s^{-1}, values calculated from activation parameters at 293.15 K. The experimental rate constants were measured in the range 283-333 K and were reproducible within ±3%. [c] kJ mol-1. At 313.15 K the maximum error is 3 kJ mol-1. [d] J K mol-1. At 313.15 K the maximum error is 8 J K mol-1. [e] Citrate buffer; total buffer concentration 0.0125 M. [f] Borate buffer; total buffer concentration 0.0125 M. [g] s^{-1}; values directly measured at 293.15 K.

Table S3. Calculated Apparent Kinetic Constants (at 293.15 K) and Activation Parameters for the Rearrangement of 3a into 6a at Various pS^+ and Citrate Buffer Concentrations in 1:1 (v:v) Dioxane/Water

pS^{+a}	0.10	0.18	0.25	0.29	0.33	0.40	0.49	0.58
$10^5(k_{A,R})_{\mathbf{3a}}{}^b$	10.1	9.44	8.91	8.51	8.17	7.50	6.65	5.79
pS^{+a}	0.71	0.80	0.89	1.11	1.21[c]	1.80[c]	2.30[c]	2.80[c]
$10^5(k_{A,R})_{\mathbf{3a}}{}^b$	4.85	4.23	3.64	2.33	1.95	0.558	0.204	0.0867
pS^{+c}	3.60	4.35	4.98	6.20				
$10^5(k_{A,R})_{\mathbf{3a}}{}^b$	0.0600	0.0604	0.0604	0.0605				
pS^{+d}	1.01	1.43	1.93	2.55	4.73	5.25	5.71	6.62
$10^5(k_{A,R})_{\mathbf{3a}}{}^b$	2.82	1.20	0.399	0.128	0.0596	0.0598	0.0594	0.0582
$\Delta H^{\#e}$	84	83	85	86	96	96	96	97
$\Delta S^{\#f}$	-47	-56	-57	-64	-35	-36	-35	-34
pS^{+g}	1.30	1.61	2.00	2.20				
$10^5(k_{A,R})_{\mathbf{3a}}{}^b$	1.63	0.802	0.355	0.250				
$\Delta H^{\#e}$	86	86	80	82				
$\Delta S^{\#f}$	-43	-50	-74	-72				

[a] NaCl/HCl buffer. [b] s^{-1}, values calculated from activation parameters at 293.15 K. The experimental rate constants were measured in the range 283-333 K and were reproducible within ±3%. [c] Citrate buffer; total buffer concentration 0.0125 M. [d] Citrate buffer; total buffer concentration 0.0250 M. [e] kJ mol^{-1}. At 313.15 K the maximum error is 3 kJ mol^{-1}. [f] J $K\ mol^{-1}$. At 313.15 K the maximum error is 8 J $K\ mol^{-1}$. [g] Citrate buffer; total buffer concentration 0.0500 M.

Table S4. Calculated Apparent Kinetic Constants (at 298.15 K) and Activation Parameters for the Rearrangement of 3a into 6a at Various pS^+ and Borate Buffer Concentrations in 1:1 (v:v) Dioxane/Water

pS^{+a}	9.16	9.60	9.88	10.19	10.45	10.79	11.10	11.45
$10^5(k_{A,R})_{\mathbf{3a}}{}^b$	0.472	1.24	2.34	4.05	7.55	14.4	29.6	61.0
pS^{+a}	11.70	11.81	11.97	12.10				
$10^5(k_{A,R})_{\mathbf{3a}}{}^b$	103	123	176	224				
pS^{+c}	9.64	9.88	10.20	10.41	10.76	11.03	11.34	11.68
$10^5(k_{A,R})_{\mathbf{3a}}{}^b$	1.63	2.73	5.01	7.98	15.5	30.0	57.1	117
$\Delta H^{\#d}$	89	89	90	88	92	89	87	87
$\Delta S^{\#e}$	-38	-35	-28	-27	-10	-14	-14	-8
pS^{+f}	9.59	9.79	10.04	10.29	10.62	10.88	11.15	11.55
$10^5(k_{A,R})_{\mathbf{3a}}{}^b$	2.03	2.90	4.88	8.13	16.4	29.6	53.5	124
$\Delta H^{\#d}$	88	90	88	91	90	89	86	86
$\Delta S^{\#e}$	-39	-31	-31	-21	-17	-14	-18	-12

[a] Total buffer concentration 0.0125 M. [b] s^{-1}, values calculated from activation parameters at 293.15 K. The experimental rate constants were measured in the range 283-333 K and were reproducible within ±3%. [c] Total buffer concentration 0.0250 M. [d] kJ mol^{-1}. At 313.15 K the maximum error is 3 kJ mol^{-1}. [e] J K^{-1} mol^{-1}. At 313.15 K the maximum error is 8 J K^{-1} mol^{-1}. [f] Total buffer concentration 0.0500 M.

Table S6. Total Energies (Hartree) and Cartesian Coordinates (Å) of the Critical Points Computed at the B3LYP Level with the DZVP Basis

13, E = -262.12829				**13(N-2)$^+$**, E = -262.43130				**13(N-4)$^+$**, E = -262.43863			
O	0.053	-0.009	0.027	N	0.006	0.000	-0.017	N	0.006	0.001	0.072
N	-0.005	0.001	1.436	C	0.081	0.000	1.288	C	0.016	0.001	1.396
C	1.353	0.063	-0.292	O	1.343	0.000	1.765	O	1.242	-0.001	1.824
C	1.256	0.078	1.779	N	2.102	-0.001	0.628	N	2.126	-0.001	0.711
N	2.153	0.120	0.731	C	1.294	-0.001	-0.420	C	1.340	0.000	-0.320
H	1.552	0.105	2.821	H	1.647	-0.001	-1.447	H	1.684	0.000	-1.348
H	1.604	0.068	-1.345	H	-0.714	0.000	2.027	H	-0.823	0.001	2.084
				H	3.115	-0.001	0.770	H	-0.818	0.002	-0.532
9, E = -317.50009				**12**, E = -317.83377				**10**, E = -317.83698			
C	0.000	-0.061	-0.083	N	0.002	-0.025	-0.039	O	0.342	0.003	-0.195
O	-0.004	-0.188	1.256	C	0.026	-0.065	1.298	N	0.012	-0.106	1.203
N	1.369	-0.114	1.658	O	1.286	-0.049	1.817	C	1.152	-0.029	1.801
C	1.984	0.045	0.514	N	2.082	0.006	0.684	N	2.207	0.122	0.906
N	1.193	0.084	-0.608	C	1.283	0.017	-0.382	C	1.648	0.136	-0.321
N	-1.204	-0.038	-0.725	N	-1.001	-0.115	2.125	H	1.269	-0.077	2.877
H	3.063	0.137	0.482	H	1.669	0.057	-1.396	H	2.219	0.257	-1.506
H	-1.150	-0.212	-1.721	H	-1.939	-0.126	1.736	H	1.638	0.246	-2.341
H	-1.976	-0.487	-0.247	H	-0.880	-0.141	3.133	H	3.222	0.357	-1.621
				H	3.086	0.021	0.853	H	3.193	0.206	1.137

11, E = -317.79517

O	0.417	-0.361	-0.238
N	0.078	-0.345	1.147
C	1.177	0.076	1.722
N	2.229	0.349	0.851
C	1.670	0.057	-0.266
H	1.243	0.198	2.797
N	2.317	0.152	-1.575
H	1.823	0.809	-2.201
H	3.282	0.493	-1.437
H	2.359	-0.764	-2.051