Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Computational Methods: Energies (in Hartree) and geometries

All data presented below come from frequency calculation output, using the following method (command line):

#freq BHandHLYP/6-311++g(3df,2p) SCRF=(smd,solvent=water)

2F-histidine (zwitterionic, τ-form):

Sum of electronic and thermal Free Energies= −647.811993 (Hartree)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.969487	0.127724	−0.105555
2	6	0	1.483660	−0.115520	−0.381304
3	1	0	1.259157	0.157045	−1.401344
4	6	0	0.613678	0.681607	0.584792
5	1	0	0.816916	0.339678	1.595863
6	1	0	0.918595	1.716648	0.526309
7	6	0	−0.839896	0.589411	0.294192
8	6	0	−1.714070	1.581136	0.028023
9	1	0	−1.595598	2.639900	−0.039738
10	6	0	−2.712618	−0.329684	−0.010413
11	9	0	−3.681265	−1.192283	−0.136245
12	7	0	−2.933868	0.968719	−0.164441
13	1	0	−3.812837	1.402848	−0.366751
14	7	0	−1.496639	−0.633062	0.265409
15	8	0	3.411414	1.224880	−0.474167
16	8	0	3.590242	−0.774372	0.477760
17	1	0	1.654813	−1.916070	0.591498
18	1	0	0.188618	−1.723025	−0.166332
19	1	0	1.555654	−2.086252	−1.027710
20	7	0	1.192131	−1.565991	−0.239930

Rotational constants (GHZ): 2.5128416 0.4435697 0.3905306

Standard basis: 6−311++G(3df,2p) (5D, 7F)

2F-histidine (zwitterionic, π-form):

Sum of electronic and thermal Free Energies= −647.809993 (Hartree)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.060744	−0.971818	0.007240
2	6	0	1.647883	0.470355	−0.326486
3	1	0	1.273847	0.469458	−1.341873
4	6	0	0.620283	1.096334	0.615418
5	1	0	0.849277	0.800765	1.634165
6	1	0	0.719372	2.173890	0.567206
7	6	0	−0.792125	0.787885	0.282696
8	6	0	−1.846371	1.595310	0.035764
9	1	0	−1.866265	2.663988	0.022946
10	6	0	−2.577680	−0.358254	−0.105670
11	9	0	−3.332625	−1.412613	−0.275761
12	7	0	−2.986101	0.851897	−0.209015
13	7	0	−1.290932	−0.491917	0.194037
14	8	0	3.264703	−1.240892	−0.106715
15	8	0	1.153445	−1.752593	0.330893
16	1	0	2.723241	2.179599	−0.830532
17	1	0	3.179022	1.519280	0.602292
18	1	0	3.624190	0.786244	−0.783968
19	7	0	2.875235	1.306913	−0.341296
20	1	0	−0.718045	−1.318960	0.258343

Rotational constants (GHZ): 1.9570109 0.5378401 0.4361949
Standard basis: 6−311++G(3df,2p) (5D, 7F)

4F-histidine (zwitterionic, τ-form):

Sum of electronic and thermal Free Energies= −647.803872 (Hartree)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.776432	0.389688	−0.104530
2	6	0	1.381465	−0.182588	−0.364443
3	1	0	1.111311	0.000938	−1.394042
4	6	0	0.344067	0.427172	0.569831
5	1	0	0.605724	0.171724	1.593213
6	1	0	0.409800	1.502103	0.482008
7	6	0	−1.043380	−0.007537	0.265534
8	6	0	−2.143607	0.733014	0.040880
9	6	0	−2.682635	−1.347118	−0.116218
10	7	0	−3.182695	−0.101536	−0.198338
11	1	0	−4.130449	0.159435	−0.390958
12	7	0	−1.413085	−1.333453	0.160851
13	8	0	2.935362	1.578871	−0.414669
14	8	0	3.615635	−0.371165	0.401225
15	1	0	1.905482	−1.879260	0.675771
16	1	0	0.456616	−2.018830	−0.128310
17	1	0	1.904393	−2.107068	−0.937969
18	7	0	1.409820	−1.657057	−0.179300
19	9	0	−2.319540	2.032647	0.027232
20	1	0	−3.287332	−2.215969	−0.266073

Rotational constants (GHZ): 1.9788549 0.5182190 0.4242283
Standard basis: 6−311++G(3df,2p) (5D, 7F)

4F-histidine (zwitterionic, π-form):

Sum of electronic and thermal Free Energies= −647.809568 (Hartree)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.253077	−0.713724	−0.023311
2	6	0	1.438601	0.559509	−0.301460
3	1	0	1.112382	0.508420	−1.331967
4	6	0	0.245251	0.801845	0.619154
5	1	0	0.529154	0.557656	1.637801
6	1	0	0.011817	1.859594	0.601927
7	6	0	−0.994860	0.087042	0.233836
8	6	0	−2.248351	0.528084	−0.011363
9	6	0	−2.384508	−1.540948	−0.224615
10	7	0	−3.115590	−0.454827	−0.289923
11	7	0	−1.118741	−1.270249	0.091931
12	8	0	3.483674	−0.611524	−0.133710
13	8	0	1.615213	−1.740133	0.250793
14	1	0	1.996550	2.523426	−0.708240
15	1	0	2.529276	1.981785	0.746190
16	1	0	3.259434	1.446394	−0.613297
17	7	0	2.365253	1.718336	−0.218802
18	1	0	−0.330893	−1.892774	0.156344
19	9	0	−2.659368	1.786632	0.015622
20	1	0	−2.736210	−2.534606	−0.401905

Rotational constants (GHZ): 1.8483307 0.5761774 0.4523899
Standard basis: 6−311++G(3df,2p) (5D, 7F)

2F-(5-methyl)-imidazole(zwitterionic, τ-form):

Sum of electronic and thermal Free Energies= −364.653544 (Hartree)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.002130	−0.950300	0.000001
2	7	0	0.811842	1.093873	−0.000002
3	6	0	−1.049221	−0.045332	0.000000
4	6	0	−2.460480	−0.493187	−0.000001
5	6	0	−0.564130	1.214192	−0.000003
6	6	0	1.049747	−0.211184	0.000000
7	1	0	−2.680177	−1.096465	0.874027
8	1	0	−3.127195	0.359000	−0.000005
9	1	0	−2.680174	−1.096473	−0.874024
10	1	0	−1.046733	2.166492	−0.000008
11	9	0	2.276278	−0.661095	0.000003
12	1	0	1.494470	1.825357	0.000019

Rotational constants (GHZ): 7.1447376 2.1146359 1.6480868
Standard basis: 6−311++G(3df,2p) (5D, 7F)

2F-(5-methyl)-imidazole(zwitterionic, π-form):

Sum of electronic and thermal Free Energies= −364.653776 (Hartree)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.033030	−0.842574	−0.000008
2	7	0	0.859825	1.195562	0.000010
3	6	0	−1.056581	0.005221	−0.000001
4	6	0	−2.451857	−0.483290	0.000004
5	6	0	−0.525315	1.245679	−0.000006
6	6	0	1.109379	−0.058847	0.000001
7	1	0	0.026441	−1.843172	−0.000023
8	1	0	−2.660223	−1.088104	0.875562
9	1	0	−3.129512	0.359355	−0.000008
10	1	0	−2.660220	−1.088127	−0.875539
11	1	0	−1.046319	2.178881	−0.000008
12	9	0	2.307343	−0.582480	0.000002

Rotational constants (GHZ): 7.2148116 2.1002679 1.6430652
Standard basis: 6−311++G(3df,2p) (5D, 7F)

4F-(5-methyl)-imidazole(zwitterionic, τ-form):

Sum of electronic and thermal Free Energies= −364.644504 (Hartree)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.214894	−1.489037	0.000003
2	7	0	1.440384	0.326775	0.000000
3	6	0	−0.631550	−0.400665	0.000001
4	6	0	−2.107608	−0.512170	0.000000
5	6	0	0.138886	0.702157	0.000000
6	6	0	1.426690	−1.019172	−0.000005
7	1	0	−2.458843	−1.046694	0.875513
8	1	0	−2.564212	0.468962	−0.000036
9	1	0	−2.458836	−1.046754	−0.875479
10	1	0	2.239224	0.929846	0.000033
11	9	0	−0.181055	1.978421	−0.000002
12	1	0	2.326696	−1.596224	−0.000008

Rotational constants (GHZ): 3.7011083 3.4875494 1.8155098
Standard basis: 6−311++G(3df,2p) (5D, 7F)

4F-(5-methyl)-imidazole(zwitterionic, π-form):

Sum of electronic and thermal Free Energies= −364.654333 (Hartree)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.396303	−1.356796	0.000132
2	7	0	1.463972	0.553624	−0.000027
3	6	0	−0.582892	−0.393072	0.000031
4	6	0	−2.035060	−0.670546	0.000033
5	6	0	0.136000	0.749298	−0.000070
6	6	0	1.586211	−0.747797	0.000113
7	1	0	0.245350	−2.346033	0.000209
8	1	0	−2.330614	−1.236324	0.876445
9	1	0	−2.586254	0.259622	−0.000084
10	1	0	−2.330577	−1.236522	−0.876265
11	1	0	2.509315	−1.286731	0.000187
12	9	0	−0.350522	1.982321	−0.000208

Rotational constants (GHZ): 3.7136609 3.4888587 1.8189207
Standard basis: 6−311++G(3df,2p) (5D, 7F)