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SUPPORTING  
INFORMATION

## Supporting Information

**Manuscript title:** Low energy tautomers and conformers of neutral and protonated arginine

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**Table S1.** The Cartesian coordinates (in Å) for the neutral structures of arginine optimized at the MP2/6-31++G\*\*+5sp(diffuse) level.

Atom	X	Y	Z
N5			
C	1.366294	1.434832	-0.405361
C	1.803657	0.301064	0.538175
C	1.907353	-1.003724	-0.262471
O	2.942037	-1.325685	-0.833684
C	-0.061536	1.295488	-0.938721
C	-1.099219	1.588978	0.152743
N	-2.401112	0.972454	-0.068565
C	-2.582157	-0.357279	0.222473
N	-3.857870	-0.815094	-0.103426
N	-1.620911	-1.069084	0.738455
N	3.066461	0.678906	1.165785
O	0.802850	-1.770841	-0.340798
H	-4.056634	-1.762247	0.184248
H	-4.610781	-0.174490	0.108189
H	-1.970533	-1.980994	1.028618
H	-2.942216	1.317390	-0.850092
H	-0.755937	1.225060	1.120158
H	-1.256510	2.665510	0.245529
H	-0.209316	1.988928	-1.771566
H	-0.224930	0.294081	-1.341459
H	1.471311	2.369473	0.153128
H	2.078808	1.475021	-1.235029
H	1.063109	0.172362	1.331939
H	3.325636	-0.013291	1.863363
H	3.797435	0.647413	0.458262
H	0.019099	-1.378459	0.133813
N3			
C	-1.271391	1.430635	0.435654
C	-0.150436	2.155424	-0.316143
C	1.243090	1.621669	0.018537
N	1.291019	0.167983	-0.091917
C	2.408661	-0.431446	-0.358005

N	2.426743	-1.803065	-0.582455
C	-1.779590	0.162086	-0.295879
C	-1.781490	-1.038423	0.657080
O	-2.796555	-1.604853	1.037858
N	-3.068513	0.436369	-0.917018
O	-0.550025	-1.429150	1.055363
N	3.662706	0.148315	-0.450117
H	-3.775432	0.519446	-0.189947
H	0.133313	-0.808563	0.647419
H	3.693277	1.155878	-0.451959
H	4.288735	-0.277382	-1.119144
H	3.211788	-2.284932	-0.164431
H	1.544124	-2.251441	-0.369969
H	-1.076808	-0.080452	-1.097867
H	-2.131186	2.096470	0.536594
H	-0.933889	1.195579	1.450196
H	-0.331977	2.079314	-1.391979
H	-0.158792	3.221262	-0.069468
H	1.969000	2.109550	-0.646580
H	1.495497	1.909380	1.047181
H	-3.351760	-0.358970	-1.482720
N4			
C	1.003836	1.567976	-0.479579
C	1.012770	1.624313	1.060979
N	2.398148	1.607038	1.523224
C	-0.377826	1.738755	-1.144796
C	-0.924884	0.486740	-1.839398
N	-1.282740	-0.562753	-0.888899
C	-0.819331	-1.847889	-0.897680
N	-0.684723	-2.483135	0.236655
N	-0.484680	-2.342906	-2.156050
C	0.143744	0.480223	1.550866
O	0.795615	-0.690461	1.522088
O	-1.053721	0.608614	1.818090
H	2.806019	0.696920	1.326460
H	-1.618729	-0.263800	0.020420
H	0.145120	-1.444974	1.345619
H	-0.483164	-3.470364	0.096662
H	-0.237661	-3.321808	-2.167938
H	-1.114985	-2.087042	-2.904085
H	0.547398	2.555282	1.391573
H	1.683970	2.355805	-0.808841
H	1.453080	0.614408	-0.779292
H	-1.114887	2.086292	-0.414359
H	-0.316141	2.518588	-1.908603
H	-1.801031	0.765304	-2.434850
H	-0.172134	0.087100	-2.521272
H	2.436101	1.734639	2.530244
N2			
C	2.590486	-0.937851	1.573370

O	2.605108	-0.001906	2.550248
O	3.551620	-1.647775	1.323741
C	1.290341	-0.967729	0.767557
H	1.107572	-2.013948	0.496635
N	0.220064	-0.375908	1.578868
H	-0.080266	-1.042960	2.286774
H	1.696969	0.384851	2.534345
C	1.537432	-0.169841	-0.521008
H	1.896202	0.830643	-0.252852
H	2.354478	-0.667684	-1.046174
C	0.295280	-0.056048	-1.417807
H	-0.404155	-0.866041	-1.196415
C	-0.421048	1.288878	-1.242677
H	0.582218	-0.163883	-2.467579
N	-1.778213	1.312119	-1.774924
H	-0.491259	1.556520	-0.189233
H	0.142819	2.079734	-1.742280
H	-1.856243	1.232937	-2.780801
C	-2.768175	0.650617	-1.074858
N	-2.521288	0.143638	0.093213
N	-3.976051	0.590629	-1.779874
H	-3.377739	-0.201543	0.523324
H	-0.618663	-0.162455	1.033054
H	-4.756969	0.252450	-1.235441
H	-4.206270	1.437323	-2.283702
N1			
H	-0.311530	-0.582972	-2.255757
N	-0.264184	-0.740114	-1.251983
C	1.126222	-0.736528	-0.805900
C	1.942146	-1.834648	-1.470579
O	3.275416	-1.562634	-1.431586
C	1.231379	-0.917848	0.721120
C	0.950611	0.321937	1.584373
C	-0.506546	0.703811	1.827721
N	-1.118175	1.302360	0.650392
C	-2.344129	1.921719	0.808766
N	-2.922736	2.256858	-0.430644
N	-2.857626	2.115474	1.981585
H	-1.056335	0.698422	-0.172007
H	-3.697973	2.900869	-0.353332
H	-2.247700	2.569500	-1.116796
H	-0.662175	-1.664567	-1.098660
H	1.577113	0.221710	-1.079155
O	1.483719	-2.857538	-1.959676
H	0.563409	-1.737540	1.012064
H	2.249583	-1.248859	0.940097
H	1.389047	0.122558	2.566985
H	1.482163	1.185508	1.172214
H	-1.073015	-0.172610	2.172527
H	-0.560013	1.440609	2.628462

H	3.729662	-2.326467	-1.829630
H	-3.714360	2.662509	1.904635
Z3			
N	-3.055078	-0.681761	0.857518
C	-2.167858	-0.036693	-0.112926
C	-1.091972	-0.953566	-0.704865
O	-0.630331	-1.862305	0.066679
C	-1.451143	1.133012	0.598473
C	-0.588151	2.045601	-0.297953
C	0.924850	1.892418	-0.107965
N	1.346429	0.534835	-0.460017
C	2.123408	-0.244030	0.283148
N	1.992003	-1.570185	0.186779
N	3.019487	0.321907	1.144561
O	-0.619877	-0.638664	-1.846799
H	-2.481582	-1.315950	1.411382
H	0.751822	0.043769	-1.163539
H	1.009419	-1.912536	-0.003011
H	2.641692	-2.165077	0.676574
H	3.604756	-0.287706	1.692854
H	3.425924	1.207971	0.887832
H	-2.771177	0.367222	-0.929669
H	-2.235491	1.718508	1.081931
H	-0.842739	0.704389	1.405167
H	-0.826987	1.876022	-1.350586
H	-0.815790	3.093859	-0.085040
H	1.454357	2.619471	-0.730990
H	1.190079	2.076590	0.936065
H	-3.717311	-1.272796	0.362614
Z2			
C	1.639652	1.321899	-0.134349
C	0.350655	1.928858	0.457040
C	-0.830502	1.910007	-0.517270
N	-1.231577	0.563485	-0.931808
C	-2.000003	-0.268637	-0.221825
N	-1.994582	-1.566682	-0.560527
C	2.053954	-0.041211	0.450040
C	0.859878	-1.001049	0.368624
O	0.102953	-1.094156	1.376236
N	3.249112	-0.492384	-0.267518
O	0.659758	-1.546999	-0.786815
N	-2.867636	0.202689	0.709407
H	2.935951	-0.901466	-1.146497
H	-0.559132	0.060638	-1.509745
H	-2.732770	1.145070	1.038386
H	-3.116512	-0.450178	1.437433
H	-2.484494	-2.178215	0.077320
H	-1.010944	-1.873629	-0.774838
H	2.306668	0.090088	1.504981
H	2.483468	1.998909	0.011170

H	1.540415	1.195397	-1.219920
H	0.073521	1.397847	1.371846
H	0.517129	2.976463	0.724478
H	-1.700896	2.426746	-0.107272
H	-0.569936	2.441618	-1.434120
H	3.686807	-1.248995	0.250970
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Z3			
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N	-3.185292	-0.590295	0.716219
C	-2.099590	-0.085328	-0.137479
C	-0.868354	-0.999826	-0.122141
O	-0.345046	-1.239105	1.002526
C	-1.744217	1.316856	0.370358
C	-0.661866	2.102657	-0.389262
C	0.795388	1.837574	0.011462
N	1.347317	0.668463	-0.680306
C	2.113355	-0.260958	-0.101789
N	2.144706	-1.480211	-0.648408
N	2.922690	0.063050	0.939054
O	-0.418928	-1.391888	-1.269369
H	-2.770600	-0.861891	1.606283
H	0.765275	0.275966	-1.420962
H	1.187046	-1.755850	-1.000770
H	2.687278	-2.181597	-0.166457
H	3.121012	-0.671547	1.601248
H	2.828689	0.982250	1.340701
H	-2.473781	-0.020342	-1.162310
H	-2.671609	1.894087	0.345837
H	-1.453068	1.227477	1.422465
H	-0.770172	1.966781	-1.471515
H	-0.833585	3.166474	-0.204123
H	1.407847	2.711456	-0.227374
H	0.837800	1.662831	1.090430
H	-3.564578	-1.441047	0.308480

**Table S2.** The Cartesian coordinates (in Å) for the protonated structures of arginine optimized at the MP2/6-31++G\*\* level.

Atom	X	Y	Z
P1			
C	-0.817938	-1.664236	-1.308789
C	-0.912883	-1.709827	0.223637
C	0.397864	-1.682177	1.012870
N	1.046561	-0.374724	0.912000
C	1.148562	0.531083	1.873579
N	1.112177	0.181125	3.177830
C	-0.373103	-0.347555	-1.978795
N	1.074531	-0.134714	-1.846628
C	-1.090099	0.843000	-1.374405
O	-2.415401	0.760983	-1.575584
O	-0.546337	1.766253	-0.776233
N	1.284221	1.822937	1.531946
H	1.561290	2.514592	2.209298
H	0.892894	2.128889	0.648782
H	1.094753	0.896043	3.887449
H	1.430653	-0.731412	3.461889
H	1.238900	-0.082511	-0.067908
H	0.186677	-1.897350	2.059022
H	1.090793	-2.443036	0.647844
H	-1.558818	-0.906105	0.589379
H	-1.416486	-2.645412	0.480944
H	-1.808061	-1.899057	-1.702259
H	-0.148051	-2.454667	-1.662030
H	-0.691343	-0.395913	-3.026354
H	1.569286	-0.877209	-2.335984
H	1.347542	0.736526	-2.297067
H	-2.832986	1.554600	-1.193048
P2			
C	-0.649571	1.594178	-1.215839
C	-0.553901	1.332234	0.288928
C	0.878989	1.129509	0.781011
N	0.934799	0.787590	2.205985
C	0.882279	-0.460319	2.688638
N	0.702596	-1.503933	1.885206
C	-0.104136	0.485247	-2.136144
N	-0.521174	0.752207	-3.514685
C	-0.679821	-0.868954	-1.716154
O	-1.671176	-1.322205	-2.469698
O	-0.276510	-1.479271	-0.725641
N	1.012626	-0.641254	4.020616
H	0.907240	-1.560936	4.418120
H	1.510212	0.036470	4.576026
H	0.821816	-2.438192	2.245220
H	0.831071	1.537201	2.876150
H	1.385548	0.331467	0.241040

H	1.468725	2.037662	0.651607
H	-0.985915	2.189919	0.810195
H	-1.159588	0.465703	0.557343
H	-0.118443	2.516958	-1.467852
H	-1.701388	1.751312	-1.471089
H	0.982031	0.412330	-2.031325
H	-0.704080	1.736275	-3.679760
H	0.171833	0.449686	-4.192414
H	-1.743933	-0.670695	-3.213372
H	0.371437	-1.417025	0.920285
P3			
H	0.582486	0.098375	-2.304080
N	0.265841	-0.258857	-1.404519
C	1.429440	-0.764651	-0.651954
C	1.757112	-2.184715	-1.095896
O	2.998553	-2.547621	-0.716033
C	1.176558	-0.766644	0.864914
C	1.069739	0.635205	1.494770
C	-0.352294	1.119633	1.755348
N	-1.074646	1.255819	0.489217
C	-2.248905	1.844961	0.362641
N	-2.760365	2.091109	-0.866473
N	-2.964158	2.244994	1.430546
H	-0.642370	0.777864	-0.342186
H	-3.760670	2.150190	-0.979577
H	-2.237897	1.793116	-1.675241
H	-0.311872	-1.071237	-1.634895
H	2.294096	-0.131311	-0.861498
O	0.969086	-2.907654	-1.686307
H	0.272686	-1.352277	1.068307
H	2.005439	-1.302091	1.329344
H	1.573400	0.629458	2.462834
H	1.591195	1.373535	0.879436
H	-0.868913	0.407141	2.406554
H	-0.321549	2.091650	2.253662
H	3.139264	-3.472278	-0.991082
H	-3.681885	2.944412	1.322454
H	-2.631150	2.071421	2.364339
P4			
C	-0.763643	1.295574	-0.761312
C	-0.702277	1.158649	0.764824
C	0.737972	1.181290	1.291216
N	0.876900	0.538993	2.600656
C	0.950462	-0.788322	2.749615
N	1.058621	-1.299394	3.996592
C	-0.804751	-0.068553	-1.463672
N	0.325479	-0.922786	-1.060902
C	-0.815943	0.147213	-2.970871
O	0.145914	-0.054453	-3.695276
O	-2.006758	0.628347	-3.387855

N	0.892314	-1.593626	1.691548
H	-1.731838	-0.573886	-1.181833
H	1.155569	-0.579980	-1.548731
H	-1.947336	0.782439	-4.348599
H	0.096491	1.866759	-1.128783
H	-1.654537	1.848457	-1.059405
H	-1.191175	0.228474	1.065898
H	-1.260559	1.968229	1.238063
H	1.421738	0.675728	0.611215
H	1.097060	2.203698	1.400763
H	0.699604	1.089127	3.429630
H	0.665078	-1.271492	0.726755
H	0.177174	-1.846695	-1.467254
H	1.122943	-2.296607	4.125543
H	1.441874	-0.731757	4.736205
H	1.110519	-2.571108	1.811521
P5			
N	-1.604910	0.856778	-3.060434
C	-1.383333	0.871121	-1.611899
C	-0.022189	1.547099	-1.373583
O	0.403832	2.307953	-2.367578
C	-1.490134	-0.489115	-0.900270
C	-1.814672	-0.396542	0.608528
C	-0.890203	-1.233224	1.488459
N	0.451050	-0.654932	1.394983
C	1.558046	-1.146422	1.922640
N	2.751669	-0.610822	1.585929
N	1.530665	-2.184117	2.777662
O	0.631043	1.422467	-0.333483
H	-2.588007	0.933642	-3.295550
H	0.533670	0.190179	0.809526
H	2.756783	0.209200	0.994532
H	3.528669	-0.701785	2.222415
H	2.372367	-2.703245	2.970904
H	0.657360	-2.617700	3.027900
H	-2.125508	1.554516	-1.185101
H	-2.280431	-1.051271	-1.400192
H	-0.562763	-1.046659	-1.067090
H	-1.761994	0.638282	0.955876
H	-2.837845	-0.728380	0.788232
H	-1.238598	-1.204575	2.524039
H	-0.869738	-2.273420	1.150076
H	-1.246641	0.009598	-3.493062
H	-0.258845	2.177887	-3.093306
P6			
C	-0.891247	-1.675130	-0.854911
C	-0.900456	-1.677834	0.685949
C	0.503540	-1.694594	1.293658
N	1.315986	-0.521895	0.942922
C	1.257668	0.682907	1.516449



N	1.899042	1.706333	0.924063
C	-1.434571	-0.395512	-1.521487
C	-0.696475	0.804206	-0.946381
O	-1.009977	1.375955	0.085965
N	-1.144205	-0.454208	-2.957190
O	0.432894	1.126041	-1.628331
N	0.656338	0.862701	2.697523
H	-1.212036	-1.401487	-3.316383
H	1.972387	-0.607614	0.179109
H	0.276111	0.085782	3.211696
H	0.323700	1.780747	2.948714
H	1.905275	2.599646	1.393369
H	1.855658	1.747988	-0.087876
H	-2.493884	-0.276633	-1.279424
H	-1.490885	-2.506023	-1.232688
H	0.124207	-1.833139	-1.235376
H	-1.457099	-0.820949	1.069682
H	-1.409202	-2.572153	1.050638
H	0.461191	-1.794098	2.379419
H	1.063172	-2.558703	0.936473
H	-1.788943	0.117453	-3.496642
H	0.366137	0.608444	-2.472651

**Table S3.** The selected stretching frequencies (in  $\text{cm}^{-1}$ ) for canonical forms of neutral arginine calculated at the B3LYP/6-31++G\*\* level. The scaled values are given after semicolon and IR intensities in brackets (in  $\text{KM/mol}$ ).

Character	N5	N3	N4	N2	N1
Stretching of XH	3117; 2997 (1539)	2832; 2722 (1963)	2758; 2651 (1502)	3398; 3266 (553)	3407; 3275 (491)
	$\nu\text{O}(3)\text{-H}$	$\nu\text{O}(3)\text{-H}$	$\nu\text{O}(3)\text{-H}$	$\nu\text{O}(3)\text{-H}; \nu\text{N}(9)\text{-H}$	$\nu\text{N}(9)\text{-H}$
			3540; 3403 (161)	3429; 3296 (68)	3746; 3601 (68)
			$\nu\text{N}(9)\text{-H}$	$\nu\text{O}(3)\text{-H}; \nu\text{N}(9)\text{-H}$	$\nu\text{O}(3)\text{-H}$

**Table S4.** The selected stretching frequencies (in  $\text{cm}^{-1}$ ) for zwitterionic forms of neutral arginine and for the lowest protonated form P1, calculated at the B3LYP/6-31++G\*\* level. The scaled values are given after semicolon and IR intensities in brackets (in  $\text{KM/mol}$ ).

Character	Z3	Z2	Z1	P1
Stretching of XH	2691; 2587 (1034)	2668; 2565 (1187)	2925; 2812 (529)	3022; 2905 (140)
	$\nu\text{N}(12)\text{H}; \nu\text{N}(9)\text{H}$	$\nu\text{N}(12)\text{H}$	$\nu\text{N}(12)\text{H}; \nu\text{N}(9)\text{H}$	$\nu\text{N}(9)\text{H}; \nu\text{C}(4)\text{H}$
	2992; 2876 (1235)	3395; 3264 (273)	3015; 2898 (72)	3042; 2924 (56)
	$\nu\text{N}(9)\text{H}; \nu\text{N}(12)\text{H}$	$\nu\text{N}(9)\text{H}$	$\nu_3\text{C}(8)\text{H}_2$	$\nu_3\text{C}(7)\text{H}_2; \nu\text{C}(6)\text{H}; \nu\text{N}(9)\text{H}$
	3025; 2908 (58)	3622; 3482 (53)	3133; 3012 (962)	3044; 2926 (822)
	$\nu\text{N}(9)\text{H};$	$\nu_3\text{N}(11)\text{H}_2$	$\nu\text{N}(9)\text{H}; \nu\text{N}(12)\text{H}$	$\nu\text{N}(9)\text{H+many}$
	3621; 3481 (62)	3657; 3515 (60)	3622; 3482 (58)	3066; 2947 (101)
	$\nu_3\text{N}(11)\text{H}_2$	$\nu\text{N}(12)\text{H}$	$\nu_3\text{N}(11)\text{H}_2$	$\nu\text{N}(9)\text{H};$
				$\nu_3\text{C}(8)\text{H}_2;$
	3666; 3524 (59)	3739; 3594 (60)	3672; 3530 (68)	$\nu_{\text{as}}\text{C}(7)\text{H}_2$
	$\nu\text{N}(12)\text{H}$	$\nu_{\text{as}}\text{N}(11)\text{H}_2$	$\nu\text{N}(12)\text{H}$	3524; 3388 (254)
	3748; 3603 (55)		3742; 3597 (62)	$\nu_3\text{N}(12)\text{H}_2$
	$\nu_{\text{as}}\text{N}(11)\text{H}_2$		$\nu_{\text{as}}\text{N}(11)\text{H}_2$	3613; 3473 (101)
				$\nu_3\text{N}(11)\text{H}_2$
				3700; 3557 (167)
				$\nu_{\text{as}}\text{N}(12)\text{H}_2$
				3735; 3590 (78)
				$\nu_{\text{as}}\text{N}(11)\text{H}_2$
				3738; 3593 (122)
				$\nu\text{O}(3)\text{-H}$

**Table S5.** The selected IR frequencies (in  $\text{cm}^{-1}$ ) for the lowest protonated form P1, calculated at the B3LYP/6-31++G\*\* level. The scaled values are given after semicolon and IR intensities in brackets (in  $\text{KM/mol}$ ).

Character	
Deformation of amino, hydroxyl, and methylene groups, and stretching of C(10)-N, and C(1)=O(2) bonds	1333; 1308 (25)
	$\delta\text{O}(3)\text{H}+\text{many}$
	1441; 1414 (31)
	many
	1505; 1477 (98)
	$\nu\text{C}(10)\text{N}(11); \nu\text{C}(10)\text{N}(12)+\text{many}$
	1653; 1622 (43)
	$\delta\text{N}(5)\text{H}_2$
	1654; 1623 (98)
	many
	1690; 1658 (312)
	$\nu\text{C}(10)\text{N}(11)+\text{many}$
	1708; 1676 (522)
	$\nu\text{C}(10)\text{N}(9); \nu\text{C}(10)\text{N}(12)+\text{many}$
	1789; 1756 (364)
$\nu\text{C}(1)\text{O}(2); \delta\text{O}(3)\text{H}$	
Stretching of XH	3022; 2905 (140)
	$\nu\text{N}(9)\text{H}; \nu\text{C}(4)\text{H}$
	3042; 2924 (56)
	$\nu_s\text{C}(7)\text{H}_2; \nu\text{C}(6)\text{H}; \nu\text{N}(9)\text{H}$
	3044; 2926 (822)
	$\nu\text{N}(9)\text{H}+\text{many}$
	3066; 2947 (101)
	$\nu\text{N}(9)\text{H}; \nu_s\text{C}(8)\text{H}_2; \nu_{\text{as}}\text{C}(7)\text{H}_2$
	3524; 3388 (254)
	$\nu_s\text{N}(12)\text{H}_2$
	3613; 3473 (101)
	$\nu_s\text{N}(11)\text{H}_2$
	3700; 3557 (167)
	$\nu_{\text{as}}\text{N}(12)\text{H}_2$
	3735; 3590 (78)
$\nu_{\text{as}}\text{N}(11)\text{H}_2$	
3738; 3593 (122)	
$\nu\text{O}(3)-\text{H}$	