Supporting Information for

The Arginine Anomaly. Arginine Radicals Are Poor Hydrogen Atom Donors in Electron Transfer Induced Dissociations

Xiaohong Chen and František Tureček*
Department of Chemistry, Bagley Hall, Box 351700, University of Washington, Seattle, WA 981951700, USA

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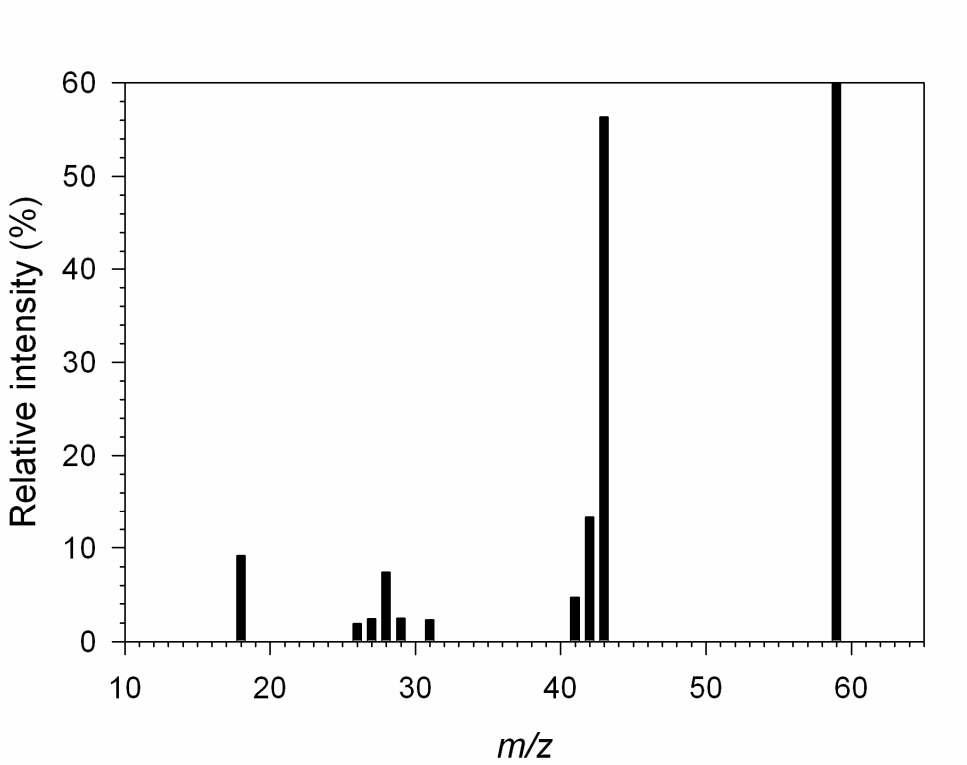


Figure S1. Collision-induced dissociation mass spectrum of guanidine cation-radical (*m/z* 59) at 10 keV laboratory collision energy. Air was used as collision gas at 50% precursor beam transmittance. The spectrum was measured as a B/E linked scam on a JEOL HX-110 double-focusing sector mass spectrometer.

Table S1. B3LYP/6-31+G(d,p) optimized structure of arginine amide conformer **1**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	3.745901	-1.660937	.685370
2	7	0	3.573538	-1.549138	-.311898
3	6	0	2.496312	-.573024	-.512949
4	6	0	2.945980	.706607	.208959
5	8	0	3.095069	.727836	1.426360
6	6	0	1.111994	-1.021373	.002222
7	6	0	-.023239	-.027405	-.277428
8	6	0	-1.383847	-.565209	.170629
9	7	0	-2.434199	.421237	-.073864
10	6	0	-3.764822	.045699	.025808
11	7	0	-4.096737	-1.184041	.204315
12	7	0	-4.631880	1.148131	-.064491
13	1	0	-2.242009	1.341260	.304488
14	1	0	-5.609853	.903289	-.140093
15	1	0	-4.361299	1.851041	-.742374
16	1	0	-5.106556	-1.308079	.147896
17	1	0	3.309315	-2.456605	-.686956
18	7	0	3.142756	1.808302	-.571824
19	1	0	3.536370	2.630728	-.135288
20	1	0	2.424767	-.378086	-1.591656
21	1	0	.879652	-1.984802	-.472283
22	1	0	1.195365	-1.204005	1.080499
23	1	0	-.069519	.203873	-1.350323
24	1	0	.186697	.918794	.241042
25	1	0	-1.649760	-1.466968	-.386260
26	1	0	-1.351579	-.852076	1.232531
27	1	0	3.183332	1.736678	-1.576595

Rotational constants (GHZ): 2.0501284 .3018419 .2792876

Table S2. B3LYP/6-31+G(d,p) optimized structure of arginine amide conformer **2**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	3.261100	-2.415811	-.729899
2	7	0	3.491118	-1.571106	-.213180
3	6	0	2.491424	-.522808	-.472963
4	6	0	2.903244	.716582	.350984
5	8	0	2.615760	.866359	1.529386
6	6	0	1.101569	-1.016521	-.060817
7	6	0	-.035124	-.077516	-.478672
8	6	0	-1.411467	-.582445	-.034985
9	7	0	-2.459036	.304494	-.513540
10	6	0	-3.644997	.184943	-.042667
11	7	0	-4.115063	-.807857	.816081
12	7	0	-4.633380	1.114302	-.384003
13	1	0	-4.301253	1.752183	-1.097083
14	1	0	4.424384	-1.279823	-.491449
15	7	0	3.676718	1.621679	-.330074
16	1	0	-5.531625	.708054	-.619888
17	1	0	3.764469	1.592691	-1.334121
18	1	0	3.941143	2.471727	.148133
19	1	0	-4.837190	-.518331	1.462973
20	1	0	2.456305	-.228570	-1.538964
21	1	0	.945507	-2.005174	-.516354
22	1	0	1.110262	-1.157303	1.025311
23	1	0	-.051218	.044404	-1.569688
24	1	0	.118562	.920007	-.050182
25	1	0	-1.558632	-1.603581	-.429240
26	1	0	-1.409778	-.667258	1.067918
27	1	0	-3.408518	-1.388078	1.245167

Rotational constants (GHZ): 2.0559461 .2972676 .2819414

Table S3. B3LYP/6-31+G(d,p) optimized structure of arginine amide conformer **3**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-2.912350	-2.008147	-1.417864
2	7	0	-2.907962	-1.005637	-1.250925
3	6	0	-2.123843	-.684873	-.046313
4	6	0	-2.088408	.853726	.076045
5	8	0	-1.129229	1.542070	-.256828
6	6	0	-.713857	-1.262614	-.183428
7	6	0	.151857	-1.084796	1.069418
8	6	0	1.630477	-1.447244	.856366
9	7	0	2.278116	-.808178	-.303343
10	6	0	2.798510	.494894	-.261935
11	7	0	1.957926	1.426609	.327565
12	7	0	3.946332	.862866	-.721698
13	1	0	2.911655	-1.432237	-.784128
14	1	0	4.515460	.059474	-.987882
15	1	0	-3.872472	-.694662	-1.180598
16	7	0	-3.238380	1.414123	.554177
17	1	0	-3.976362	.861767	.962414
18	1	0	-3.274952	2.418396	.658932
19	1	0	2.346874	2.358514	.255322
20	1	0	-2.584748	-1.080501	.879353
21	1	0	-.804824	-2.332620	-.419046
22	1	0	-.230990	-.787861	-1.041529
23	1	0	-.223805	-1.718716	1.885030
24	1	0	.090873	-.054144	1.428485
25	1	0	2.182956	-1.231377	1.782145
26	1	0	1.707287	-2.526183	.678595
27	1	0	.978595	1.388694	.054053

Rotational constants (GHZ): 1.5708306 .4817713 .4167084

Table S4. B3LYP/6-31+G(d,p) optimized structure of arginine amide conformer **4**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	2.789610	-2.181784	1.294088
2	7	0	2.927036	-1.179547	1.194851
3	6	0	2.193911	-.672198	.022264
4	6	0	2.341023	.864412	.030148
5	8	0	1.518250	1.626431	.518925
6	6	0	.728466	-1.105635	.105291
7	6	0	-.113072	-.699884	-1.110144
8	6	0	-1.558495	-1.239076	-1.056963
9	7	0	-2.273147	-.896573	.162969
10	6	0	-2.917261	.211051	.227017
11	7	0	-2.970885	1.200170	-.750978
12	7	0	-3.756822	.461155	1.318475
13	1	0	-3.682574	-.281744	2.003214
14	1	0	3.925527	-1.003744	1.128549
15	7	0	3.510010	1.321223	-.522358
16	1	0	-3.652156	1.377069	1.740460
17	1	0	4.121209	.722527	-1.055468
18	1	0	3.668418	2.318471	-.550724
19	1	0	-3.516009	2.026043	-.553446
20	1	0	2.615719	-1.043903	-.931864
21	1	0	.706657	-2.200250	.207456
22	1	0	.291602	-.690159	1.016306
23	1	0	.351574	-1.074141	-2.034674
24	1	0	-.119439	.395200	-1.182237
25	1	0	-2.096330	-.902675	-1.959629
26	1	0	-1.514980	-2.334734	-1.109250
27	1	0	-2.135614	1.365374	-1.290582

Rotational constants (GHZ): 1.5602344 .4167217 .3872098

Table S5. B3LYP/6-31+G(d,p) optimized structure of arginine amide conformer **5**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-3.300350	-2.069935	-.963490
2	7	0	-3.223963	-1.056423	-.981338
3	6	0	-2.281912	-.590755	.047721
4	6	0	-2.264160	.952705	-.008963
5	8	0	-1.576164	1.582460	-.797778
6	6	0	-.887525	-1.159353	-.236307
7	6	0	.114496	-.947055	.905997
8	6	0	1.514585	-1.511016	.594260
9	7	0	2.289100	-.762647	-.385120
10	6	0	3.023492	.370227	-.043959
11	7	0	3.603639	.974944	-1.161519
12	7	0	3.215665	.881233	1.121527
13	1	0	1.910386	-.741319	-1.323238
14	1	0	2.634756	.443926	1.833122
15	1	0	-4.154429	-.670747	-.845070
16	7	0	-3.127545	1.566843	.860263
17	1	0	-3.574764	1.064722	1.611424
18	1	0	-3.135581	2.577031	.886678
19	1	0	4.212660	1.737346	-.892892
20	1	0	-2.585770	-.894593	1.067593
21	1	0	-.991952	-2.237037	-.427119
22	1	0	-.533535	-.694932	-1.162545
23	1	0	-.257603	-1.442562	1.814380
24	1	0	.203618	.121595	1.136171
25	1	0	2.110754	-1.567689	1.510660
26	1	0	1.421684	-2.541181	.227511
27	1	0	4.037320	.339529	-1.820155

Rotational constants (GHZ): 1.4934083 .4158467 .3796704

Table S6. B3LYP/6-31+G(d,p) optimized structure of protonated arginine amide **1H**$^+$.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-2.784662	1.763284	1.803732
2	7	0	-2.739925	.796057	1.493971
3	6	0	-2.102004	.696476	.174186
4	6	0	-2.074622	-.796324	-.213561
5	8	0	-1.042030	-1.480051	-.210107
6	6	0	-.685177	1.274415	.272006
7	6	0	.094326	1.260755	-1.049850
8	6	0	1.591069	1.564676	-.905273
9	7	0	2.331485	.814619	.143886
10	6	0	2.562938	-.507052	.215394
11	7	0	1.704440	-1.399170	-.275723
12	7	0	3.699909	-.928231	.807627
13	1	0	2.912379	1.380648	.747411
14	1	0	4.494150	-.315809	.920320
15	1	0	-3.685274	.425207	1.507695
16	7	0	-3.264756	-1.336187	-.548444
17	1	0	3.788600	-1.873626	1.150574
18	1	0	-4.108934	-.788958	-.626500
19	1	0	-3.308520	-2.319268	-.782345
20	1	0	1.993631	-2.366253	-.330060
21	1	0	-2.654018	1.230788	-.621401
22	1	0	-.764120	2.304991	.641026
23	1	0	-.156361	.709201	1.045843
24	1	0	-.303071	2.020091	-1.734738
25	1	0	-.032014	.305200	-1.563850
26	1	0	2.094348	1.407049	-1.865640
27	1	0	1.732139	2.613080	-.631141
28	1	0	.680718	-1.242514	-.286705

Rotational constants (GHZ): 1.4975563 .5026549 .4367719

Table S7. B3LYP/6-31+G(d,p) optimized structure of protonated arginine amide cation **2H**$^{+}$.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-2.879911	2.389361	.583789
2	7	0	-2.226817	1.633739	.774454
3	6	0	-2.361491	.563745	-.216241
4	6	0	-3.607627	-.307082	.048750
5	8	0	-3.824176	-.739508	1.175669
6	6	0	-1.120717	-.355326	-.157435
7	6	0	.184172	.407579	-.415654
8	6	0	1.410605	-.453627	-.112099
9	7	0	2.646018	.334089	-.312416
10	6	0	3.877201	-.065156	-.000454
11	7	0	4.100125	-1.324882	.401688
12	7	0	4.911762	.790969	-.078880
13	1	0	2.538810	1.252374	-.724423
14	1	0	4.766720	1.777503	-.234393
15	1	0	-2.469858	1.261035	1.692443
16	7	0	-4.406842	-.581148	-1.017697
17	1	0	5.866606	.469742	-.019085
18	1	0	-4.278775	-.145590	-1.917861
19	1	0	-5.242275	-1.130690	-.865658
20	1	0	4.991055	-1.604178	.784718
21	1	0	-2.421224	1.026513	-1.209780
22	1	0	-1.099998	-.809209	.841484
23	1	0	-1.238039	-1.174959	-.877493
24	1	0	.189370	1.299716	.220645
25	1	0	.223355	.739553	-1.462516
26	1	0	1.380794	-.792231	.930140
27	1	0	1.433951	-1.332645	-.769616
28	1	0	3.370244	-2.020391	.371015

Rotational constants (GHZ): 2.6288955 .2617447 .2541810

Table S8. B3LYP/6-31+G(d,p) optimized structure of protonated arginine amide cation **3H**$^+$.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-3.474524	2.398797	-.653707
2	7	0	-3.525234	1.576605	-.059576
3	6	0	-2.539637	.561146	-.450233
4	6	0	-2.892803	-.774503	.243119
5	8	0	-2.175527	-1.287152	1.095875
6	6	0	-1.147766	1.045908	-.021109
7	6	0	.006062	.154524	-.502017
8	6	0	1.328170	.580158	.137977
9	7	0	2.406432	-.352659	-.253537
10	6	0	3.704999	-.176832	-.019256
11	7	0	4.129334	.865787	.709589
12	7	0	4.610441	-1.032656	-.527573
13	1	0	2.114842	-1.246761	-.629027
14	1	0	4.347152	-1.732226	-1.205695
15	1	0	-4.480460	1.235202	-.068130
16	7	0	-4.063072	-1.342943	-.159609
17	1	0	5.563298	-1.047442	-.195305
18	1	0	-4.605174	-.991958	-.934378
19	1	0	-4.343708	-2.216616	.264244
20	1	0	5.107575	1.109104	.758061
21	1	0	-2.532768	.365914	-1.540024
22	1	0	-1.012604	2.066079	-.402562
23	1	0	-1.148656	1.103757	1.071756
24	1	0	.100061	.197455	-1.595038
25	1	0	-.205599	-.880312	-.211423
26	1	0	1.610463	1.588171	-.187132
27	1	0	1.222986	.573133	1.230314
28	1	0	3.481873	1.433579	1.235096

Rotational constants (GHZ): 2.2450593 .2959019 .2759728

Table S9. B3LYP/6-31+G(d,p) optimized structure of arginine amide radical **1H**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-3.068032	-1.930723	-1.410549
2	7	0	-3.018844	-.929181	-1.244568
3	6	0	-2.186201	-.642734	-.064167
4	6	0	-2.079816	.893874	.047938
5	8	0	-1.175862	1.551644	-.453091
6	6	0	-.806149	-1.281133	-.233054
7	6	0	.076091	-1.184183	1.017667
8	6	0	1.529899	-1.617819	.771609
9	7	0	2.215992	-.835613	-.268398
10	6	0	2.818708	.406782	.065984
11	7	0	1.904374	1.395487	.465246
12	7	0	3.900704	.854481	-.732469
13	1	0	2.852718	-1.404987	-.810116
14	1	0	4.658704	.187829	-.823279
15	1	0	-3.967694	-.581806	-1.136561
16	7	0	-3.118075	1.487762	.712700
17	1	0	3.629893	1.220747	-1.652812
18	1	0	-3.771165	.953429	1.264485
19	1	0	-3.093306	2.490227	.837020
20	1	0	2.344479	2.298076	.587923
21	1	0	-2.639540	-1.017839	.873506
22	1	0	-.948985	-2.338453	-.500111
23	1	0	-.306285	-.799850	-1.077841
24	1	0	-.331471	-1.816742	1.819352
25	1	0	.086102	-.158054	1.397753
26	1	0	2.082927	-1.567704	1.722601
27	1	0	1.539662	-2.663432	.439108
28	1	0	1.034629	1.456857	-.069192

Rotational constants (GHZ): 1.4853547 .4776734 .4112511

Table S10. B3LYP/6-31+G(d,p) optimized structure of arginine amide radical **2H**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	3.180896	2.579340	-.153615
2	7	0	3.482012	1.618421	-.292290
3	6	0	2.492402	.680852	.264047
4	6	0	3.014492	-.745359	-.012329
5	8	0	2.703319	-1.401371	-.995909
6	6	0	1.131633	.915718	-.396566
7	6	0	-.009191	.098180	.221417
8	6	0	-1.356079	.396979	-.440063
9	7	0	-2.423863	-.436124	.130895
10	6	0	-3.768653	-.089362	-.140623
11	7	0	-4.138586	1.149622	.416762
12	7	0	-4.748520	-1.108938	-.108052
13	1	0	-2.258792	-1.422854	-.036783
14	1	0	-4.531960	-1.917490	-.679795
15	1	0	4.394963	1.509989	.140456
16	7	0	3.912022	-1.208126	.915425
17	1	0	-5.036718	-1.399757	.833384
18	1	0	4.039025	-.753755	1.806554
19	1	0	4.275206	-2.143817	.799432
20	1	0	-5.112759	1.368098	.248812
21	1	0	2.373862	.791075	1.359074
22	1	0	.897933	1.986641	-.313132
23	1	0	1.232375	.687428	-1.462362
24	1	0	-.091883	.303985	1.297045
25	1	0	.216505	-.971105	.116387
26	1	0	-1.637653	1.441131	-.279153
27	1	0	-1.278143	.249501	-1.529953
28	1	0	-3.898486	1.256532	1.406447

Rotational constants (GHZ): 2.1259241 .2882596 .2680717

Table S11. B3LYP/6-31+G(d,p) optimized structure of arginine amide radical **4H**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.479526	0.501061	2.157936
2	7	0	1.336653	0.180019	1.717019
3	6	0	1.175037	0.110050	0.249801
4	6	0	2.467278	-0.502949	-0.320514
5	8	0	3.413113	0.153231	-0.732675
6	6	0	0.940981	1.504784	-0.337623
7	6	0	-0.341287	2.231290	0.108805
8	6	0	-1.691787	1.677953	-0.395428
9	7	0	-2.255754	0.534990	0.336279
10	6	0	-2.061728	-0.794885	-0.085729
11	7	0	-2.523428	-1.037084	-1.393177
12	7	0	-2.260685	-1.832330	0.858344
13	1	0	-2.253788	0.645247	1.342715
14	1	0	-1.791228	-1.681879	1.744845
15	1	0	1.561164	-0.731016	2.108388
16	7	0	2.497112	-1.876144	-0.277149
17	1	0	-3.245082	-2.079932	1.019500
18	1	0	1.647542	-2.410231	-0.168246
19	1	0	3.295415	-2.338440	-0.690077
20	1	0	-2.396941	-2.001333	-1.675012
21	1	0	0.335771	-0.543719	-0.043879
22	1	0	1.810499	2.118286	-0.082206
23	1	0	0.931928	1.417485	-1.431405
24	1	0	-0.268080	3.261877	-0.263335
25	1	0	-0.374636	2.330444	1.204065
26	1	0	-2.430354	2.487868	-0.351436
27	1	0	-1.612879	1.377285	-1.444132
28	1	0	-3.482007	-0.722471	-1.571406

Rotational constants (GHZ): 1.1880221 0.5578412 0.4649525

Table S12. B3LYP/6-31+G(d,p) optimized structure of arginine amide radical **9**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-2.865606	1.617867	1.892495
2	7	0	-2.597341	.689456	1.573440
3	6	0	-1.991506	.746768	.220599
4	6	0	-2.029699	-.621842	-.440322
5	8	0	-1.155969	-1.601919	-.029327
6	6	0	-.561823	1.292556	.354372
7	6	0	.197902	1.383901	-.973736
8	6	0	1.710880	1.606933	-.830270
9	7	0	2.388285	.765996	.169240
10	6	0	2.465308	-.603434	.105966
11	7	0	1.643568	-1.298485	-.615562
12	7	0	3.508959	-1.145872	.863644
13	1	0	3.172717	1.215035	.618020
14	1	0	3.833395	-.596249	1.649496
15	1	0	-3.432677	.109733	1.551336
16	7	0	-3.330659	-1.162603	-.596639
17	1	0	3.380446	-2.117142	1.113301
18	1	0	-3.939905	-.569490	-1.150421
19	1	0	-3.297569	-2.097672	-.989521
20	1	0	1.861366	-2.291973	-.556466
21	1	0	-2.563419	1.420694	-.446788
22	1	0	-.607142	2.279080	.837030
23	1	0	-.030163	.639668	1.052952
24	1	0	-.190569	2.213274	-1.580937
25	1	0	.032487	.474661	-1.554297
26	1	0	2.183464	1.473545	-1.813865
27	1	0	1.903083	2.636574	-.508828
28	1	0	-.228207	-1.360982	-.257396

Rotational constants (GHZ): 1.4314785 .5174981 .4502977

Table S13. B3LYP/6-31+G(d,p) optimized structure of arginine amide radical **13**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	3.017463	-2.464379	-.615107
2	7	0	3.360914	-1.555595	-.316125
3	6	0	2.360679	-.483753	-.551278
4	6	0	2.846790	.747929	.189453
5	8	0	3.351857	.502810	1.446449
6	6	0	.988186	-.974905	-.058347
7	6	0	-.153934	.009911	-.329231
8	6	0	-1.505661	-.528761	.142783
9	7	0	-2.562345	.451810	-.098432
10	6	0	-3.889263	.082080	.050082
11	7	0	-4.217513	-1.141418	.274025
12	7	0	-4.758196	1.182931	-.047495
13	1	0	-2.357250	1.382698	.244712
14	1	0	-4.505895	1.865077	-.753119
15	1	0	4.220882	-1.361875	-.823716
16	7	0	3.656322	1.655286	-.543286
17	1	0	-5.737754	.936451	-.090565
18	1	0	3.160916	2.118077	-1.298300
19	1	0	4.089987	2.341206	.066542
20	1	0	-5.228789	-1.264456	.250281
21	1	0	2.275254	-.223681	-1.618674
22	1	0	.764900	-1.932106	-.551466
23	1	0	1.055097	-1.183435	1.016726
24	1	0	-.214619	.231469	-1.403381
25	1	0	.071139	.958330	.177745
26	1	0	-1.776759	-1.438265	-.399264
27	1	0	-1.459360	-.802962	1.207649
28	1	0	3.574869	-.450734	1.476765

Rotational constants (GHZ): 2.1455053 .2818343 .2645218

Table S14. B3LYP/6-31+G(d,p) optimized structure of arginine amide radical **14**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-3.324046	1.536119	-1.114064
2	7	0	-2.991460	0.584690	-1.031951
3	6	0	-2.104506	0.318629	-0.005340
4	6	0	-1.767845	-1.051424	0.293127
5	8	0	-1.063476	-1.375387	1.270061
6	6	0	-1.466031	1.471794	0.707161
7	6	0	-0.260653	2.143804	-0.019161
8	6	0	1.119980	1.593838	0.353685
9	7	0	1.308532	0.192370	-0.034739
10	6	0	2.674971	-0.306455	0.139348
11	7	0	3.515648	0.353374	-0.846035
12	7	0	2.730059	-1.765177	0.045137
13	1	0	0.686167	-0.401135	0.512582
14	1	0	2.267676	-2.198634	0.842864
15	1	0	-3.702696	-0.111116	-1.223011
16	7	0	-2.324437	-2.030586	-0.542899
17	1	0	2.238219	-2.070271	-0.794245
18	1	0	-2.315702	-1.833135	-1.537279
19	1	0	-1.977414	-2.956290	-0.322455
20	1	0	4.455911	-0.030469	-0.804373
21	1	0	3.082220	-0.050673	1.134085
22	1	0	-2.241515	2.233469	0.871927
23	1	0	-1.149306	1.125950	1.696334
24	1	0	-0.263268	3.210130	0.240209
25	1	0	-0.396733	2.078812	-1.105595
26	1	0	1.885456	2.182312	-0.159450
27	1	0	1.279142	1.741593	1.439832
28	1	0	3.139817	0.182622	-1.777362

Rotational constants (GHZ): 1.2593591 0.5507609 0.4380077

Table S15. B3LYP/6-31+G(d,p) optimized structure of transition state for the N---H bond dissociation in **1H** (**TS1**).

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	3.010538	2.562285	.050990
2	7	0	3.334777	1.605184	-.061828
3	6	0	2.264653	.658121	.295302
4	6	0	2.829114	-.764022	.093516
5	8	0	2.736465	-1.386408	-.955272
6	6	0	1.041582	.901982	-.592424
7	6	0	-.179892	.063669	-.196895
8	6	0	-1.392605	.371416	-1.086291
9	7	0	-2.582582	-.414250	-.768197
10	6	0	-3.476019	-.038916	.199816
11	7	0	-3.244439	1.008333	.951244
12	7	0	-4.610439	-.837555	.309675
13	1	0	-2.555205	-1.394025	-1.015393
14	1	0	-4.682119	-1.657659	-.277366
15	1	0	4.155447	1.484906	.525746
16	7	0	3.503724	-1.263326	1.178003
17	1	0	-4.975642	-.960990	1.243653
18	1	0	3.419498	-.844504	2.091579
19	1	0	3.869269	-2.203346	1.116582
20	1	0	-4.065728	1.266005	1.493707
21	1	0	1.951276	.753031	1.351476
22	1	0	.785550	1.968658	-.524964
23	1	0	1.333225	.699460	-1.628455
24	1	0	-.458417	.258608	.845954
25	1	0	.064484	-1.002910	-.281918
26	1	0	-1.672400	1.423675	-.989125
27	1	0	-1.146517	.182037	-2.137774
28	1	0	-2.253265	.713838	2.237068

Rotational constants (GHZ): 1.8490221 .3222256 .3092608

Table S16. B3LYP/6-31+G(d,p) optimized structure of transition state for N---C_δ bond dissociation in **1H** (**TS2**).

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-3.082779	-1.909248	-1.366008
2	7	0	-3.067405	-.912848	-1.166638
3	6	0	-2.209819	-.635333	-.001649
4	6	0	-2.078672	.899242	.097639
5	8	0	-1.177178	1.545215	-.426413
6	6	0	-.846419	-1.303269	-.184843
7	6	0	.070167	-1.192134	1.042876
8	6	0	1.454396	-1.739278	.797771
9	7	0	2.207873	-.732011	-.684791
10	6	0	2.733154	.457998	-.391365
11	7	0	1.876590	1.499495	-.034177
12	7	0	4.074608	.629906	.037843
13	1	0	2.947156	-1.395928	-.902347
14	1	0	4.752775	.161126	-.550086
15	1	0	-4.025032	-.606299	-1.020090
16	7	0	-3.090691	1.512653	.782333
17	1	0	4.348834	1.592396	.197666
18	1	0	-3.750218	.990566	1.337894
19	1	0	-3.055517	2.516199	.893552
20	1	0	2.224467	2.430127	-.231100
21	1	0	-2.655065	-.995879	.945549
22	1	0	-1.017626	-2.366338	-.408808
23	1	0	-.350720	-.867312	-1.055054
24	1	0	-.399616	-1.720149	1.892314
25	1	0	.157066	-.143953	1.352079
26	1	0	2.167745	-1.587756	1.607633
27	1	0	1.489742	-2.748611	.383207
28	1	0	.922555	1.385629	-.369664

Rotational constants (GHZ): 1.4913054 .4720121 .4027812

Table S17. B3LYP/6-31+G(d,p) optimized structure of transition state for N---C_δ bond dissociation in **2H** (**TS3**).

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-3.430686	-2.471507	-.484050
2	7	0	-3.652643	-1.479906	-.512362
3	6	0	-2.609283	-.700211	.175243
4	6	0	-2.984148	.788911	.021146
5	8	0	-2.604955	1.492367	-.904159
6	6	0	-1.243939	-1.004007	-.449602
7	6	0	-.054505	-.350105	.282435
8	6	0	1.272413	-.678730	-.342787
9	7	0	2.601902	.399884	.666947
10	6	0	3.847487	.293249	.229996
11	7	0	4.563819	-.852698	.581618
12	7	0	4.377770	.983322	-.883885
13	1	0	2.219441	1.318869	.454243
14	1	0	3.797240	1.754007	-1.189522
15	1	0	-4.566582	-1.351021	-.086721
16	7	0	-3.840312	1.258022	.985560
17	1	0	5.342689	1.281777	-.783931
18	1	0	-4.010213	.746075	1.837464
19	1	0	-4.101363	2.233593	.954363
20	1	0	5.502250	-.938322	.219494
21	1	0	-2.556654	-.926638	1.257284
22	1	0	-1.108502	-2.094323	-.454063
23	1	0	-1.269177	-.674769	-1.492856
24	1	0	-.044994	-.663784	1.335497
25	1	0	-.206016	.738661	.278231
26	1	0	1.674280	-1.670930	-.152342
27	1	0	1.410995	-.348514	-1.372700
28	1	0	4.465030	-1.127124	1.549158

Rotational constants (GHZ): 1.9838604 .2783913 .2632255

Table S18. B3LYP/6-31+G(d,p) optimized structure of transition state for N---H---O migration in **1H** (**TS4**).

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	3.479401	1.665420	-1.164420
2	7	0	3.014375	.757926	-1.207443
3	6	0	2.089380	.590013	-.055722
4	6	0	1.761132	-.869093	.141503
5	8	0	.713115	-1.453162	-.364639
6	6	0	.825708	1.426088	-.302861
7	6	0	-.077055	1.508220	.936657
8	6	0	-1.562803	1.763267	.647955
9	7	0	-2.218874	.830805	-.278670
10	6	0	-2.418203	-.501975	-.081269
11	7	0	-1.560248	-1.232911	.634154
12	7	0	-3.517779	-1.074405	-.699238
13	1	0	-2.620731	1.229220	-1.116402
14	1	0	-4.149069	-.463341	-1.201276
15	1	0	3.736622	.042908	-1.172702
16	7	0	2.803027	-1.674947	.645299
17	1	0	-3.368377	-1.972911	-1.146037
18	1	0	3.291880	-1.303902	1.457941
19	1	0	2.507304	-2.633934	.789915
20	1	0	-1.927732	-2.155300	.847927
21	1	0	2.567146	.957237	.879046
22	1	0	1.122047	2.431810	-.627716
23	1	0	.292903	.964612	-1.139809
24	1	0	.259450	2.313888	1.603350
25	1	0	.002899	.582367	1.513336
26	1	0	-2.116879	1.762241	1.596493
27	1	0	-1.691746	2.753816	.196722
28	1	0	-.442500	-1.293236	.224438

Rotational constants (GHZ): 1.4021531 .5634260 .4598675

Table S19. B3LYP/6-31+G(d,p) optimized structure of transition state for C_α---C_β dissociation in **9** (**TS5**).

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-0.877045	-0.738521	2.882698
2	7	0	-0.551705	-0.647128	1.925279
3	6	0	-1.624380	-0.235132	1.056787
4	6	0	-1.810209	-0.862330	-0.160520
5	8	0	-0.876289	-1.699545	-0.701357
6	6	0	-1.168370	1.937306	0.510436
7	6	0	-0.247068	2.016535	-0.677999
8	6	0	1.248309	1.931002	-0.338788
9	7	0	1.696811	0.748481	0.399567
10	6	0	2.006501	-0.424419	-0.248570
11	7	0	1.622217	-0.658238	-1.471530
12	7	0	2.754522	-1.298091	0.518172
13	1	0	1.240767	0.595725	1.299732
14	1	0	3.049216	-1.012552	1.439720
15	1	0	-0.195892	-1.553227	1.626373
16	7	0	-2.954188	-0.703094	-0.945751
17	1	0	2.688584	-2.287880	0.338797
18	1	0	-3.550602	0.073796	-0.688861
19	1	0	-2.770856	-0.735897	-1.942559
20	1	0	2.101909	-1.472985	-1.855299
21	1	0	-2.494455	0.173832	1.557509
22	1	0	-2.197630	2.251091	0.332631
23	1	0	-0.779531	2.264462	1.475828
24	1	0	-0.386461	2.972357	-1.214186
25	1	0	-0.493587	1.237988	-1.412714
26	1	0	1.835888	1.974992	-1.259044
27	1	0	1.523009	2.798773	0.274461
28	1	0	-0.085299	-1.216875	-1.072471

Rotational constants (GHZ): 1.0996542 0.7156155 0.6072159

Table S20. B3LYP/6-31+G(d,p) optimized structure of transition state for C_α---C_β dissociation in **13** (**TS6**).

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	3.181080	-2.382940	-0.010846
2	7	0	3.698841	-1.521331	-0.153146
3	6	0	2.860454	-0.451069	-0.650807
4	6	0	3.122801	0.772462	-0.060650
5	8	0	3.793719	0.838879	1.114792
6	6	0	0.877988	-1.290031	0.062519
7	6	0	-0.178678	-0.238742	-0.132219
8	6	0	-1.599980	-0.717710	0.215990
9	7	0	-2.571081	0.360128	0.019690
10	6	0	-3.927646	0.080098	0.032888
11	7	0	-4.358686	-1.130457	0.092542
12	7	0	-4.708001	1.250781	0.001891
13	1	0	-2.332398	1.229387	0.482160
14	1	0	-4.361114	1.976283	-0.615026
15	1	0	4.486085	-1.717496	-0.767031
16	7	0	2.706764	2.009754	-0.515437
17	1	0	-5.696929	1.085047	-0.128934
18	1	0	1.971649	1.991839	-1.208505
19	1	0	2.555802	2.696311	0.213533
20	1	0	-5.371104	-1.169063	-0.017560
21	1	0	2.516255	-0.457514	-1.683853
22	1	0	0.821833	-2.156816	-0.598389
23	1	0	1.141566	-1.534568	1.091448
24	1	0	-0.189626	0.105130	-1.177349
25	1	0	0.062239	0.638369	0.487940
26	1	0	-1.896412	-1.546692	-0.430029
27	1	0	-1.631441	-1.096447	1.247841
28	1	0	4.088265	-0.084020	1.271155

Rotational constants (GHZ): 1.9459999 0.2753592 0.2513413

Table S21. B3LYP/6-31+G(d,p) optimized structure of transition state for C...H...C migration in **4H** (**TS7**).

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.208224	0.764796	2.290532
2	7	0	1.070268	0.571708	1.791956
3	6	0	0.918679	0.510368	0.358490
4	6	0	2.115069	-0.079835	-0.329500
5	8	0	2.689834	0.448161	-1.277601
6	6	0	0.394583	1.805415	-0.245569
7	6	0	-1.063689	2.147580	0.129635
8	6	0	-2.162599	1.219823	-0.434200
9	7	0	-2.293435	-0.116064	0.178620
10	6	0	-1.251827	-1.065237	-0.087761
11	7	0	-1.283413	-1.462067	-1.453898
12	7	0	-1.126538	-2.148734	0.853405
13	1	0	-2.483972	-0.050934	1.173691
14	1	0	-1.087133	-1.831197	1.818656
15	1	0	1.546909	-0.224752	2.197923
16	7	0	2.531481	-1.301354	0.184964
17	1	0	-1.878432	-2.836274	0.760030
18	1	0	1.832894	-1.915172	0.587809
19	1	0	3.248208	-1.761917	-0.361159
20	1	0	-0.586233	-2.164787	-1.671183
21	1	0	-0.040289	-0.356426	0.070684
22	1	0	1.050008	2.629585	0.066057
23	1	0	0.481550	1.731044	-1.334052
24	1	0	-1.272761	3.157042	-0.248909
25	1	0	-1.178800	2.221460	1.222287
26	1	0	-3.134837	1.712644	-0.320466
27	1	0	-2.003460	1.067516	-1.505986
28	1	0	-2.210391	-1.761030	-1.757006

Rotational constants (GHZ): 1.1066563 0.7360304 0.5928851

Table S22. B3LYP/6-31+G(d,p) optimized structure of transition state for C_α---C_β dissociation in in **14** (**TS8**).

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-3.739462	1.633485	-0.527812
2	7	0	-3.483321	0.653460	-0.568212
3	6	0	-2.377697	0.337887	0.258108
4	6	0	-1.873056	-1.061445	0.178909
5	8	0	-0.961180	-1.484515	0.897858
6	6	0	-1.665730	1.268260	0.957744
7	6	0	0.094022	2.255478	-0.431921
8	6	0	1.374394	1.684914	0.083213
9	7	0	1.504792	0.257881	-0.222694
10	6	0	2.745208	-0.363296	0.245096
11	7	0	3.840869	0.208269	-0.519995
12	7	0	2.680051	-1.820521	0.149067
13	1	0	0.723229	-0.257227	0.180010
14	1	0	1.990998	-2.192638	0.801454
15	1	0	-4.302966	0.080426	-0.387328
16	7	0	-2.507693	-1.867505	-0.734919
17	1	0	2.374553	-2.081679	-0.788102
18	1	0	-2.975672	-1.435319	-1.520113
19	1	0	-2.091506	-2.776328	-0.883511
20	1	0	4.711060	-0.251188	-0.265208
21	1	0	2.942765	-0.135539	1.308317
22	1	0	-2.067211	2.262101	1.121172
23	1	0	-0.861965	0.936553	1.599898
24	1	0	-0.143659	3.282275	-0.164996
25	1	0	-0.268507	1.910323	-1.396337
26	1	0	2.227349	2.200113	-0.384761
27	1	0	1.468534	1.895737	1.168227
28	1	0	3.676179	0.053151	-1.513399

Rotational constants (GHZ): 1.3265480 0.4847511 0.3884010

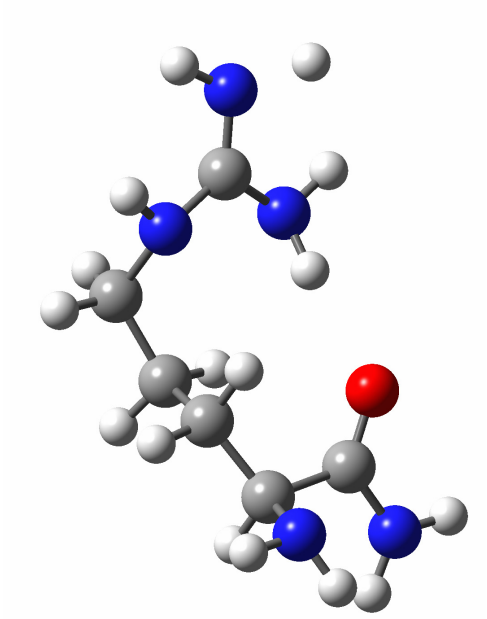


Figure S2. B3LYP/6-31+G(d,p) optimized structure of the transition state for N---H bond dissociation in arginine amide radical **1H**.

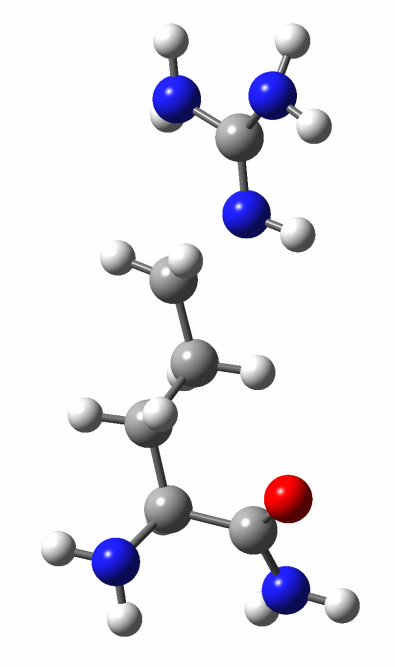


Figure S3. B3LYP/6-31+G(d,p) optimized structure of the transition state for N---C_{δ} bond dissociation in **2H**.

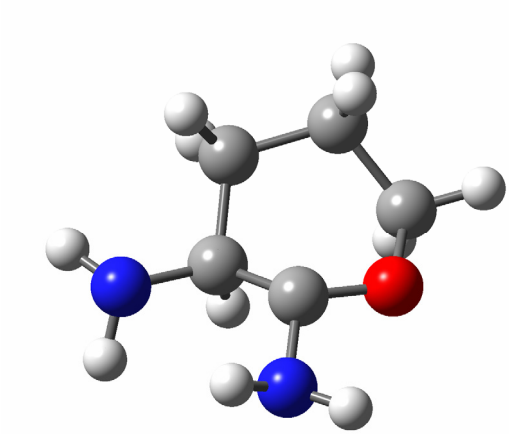
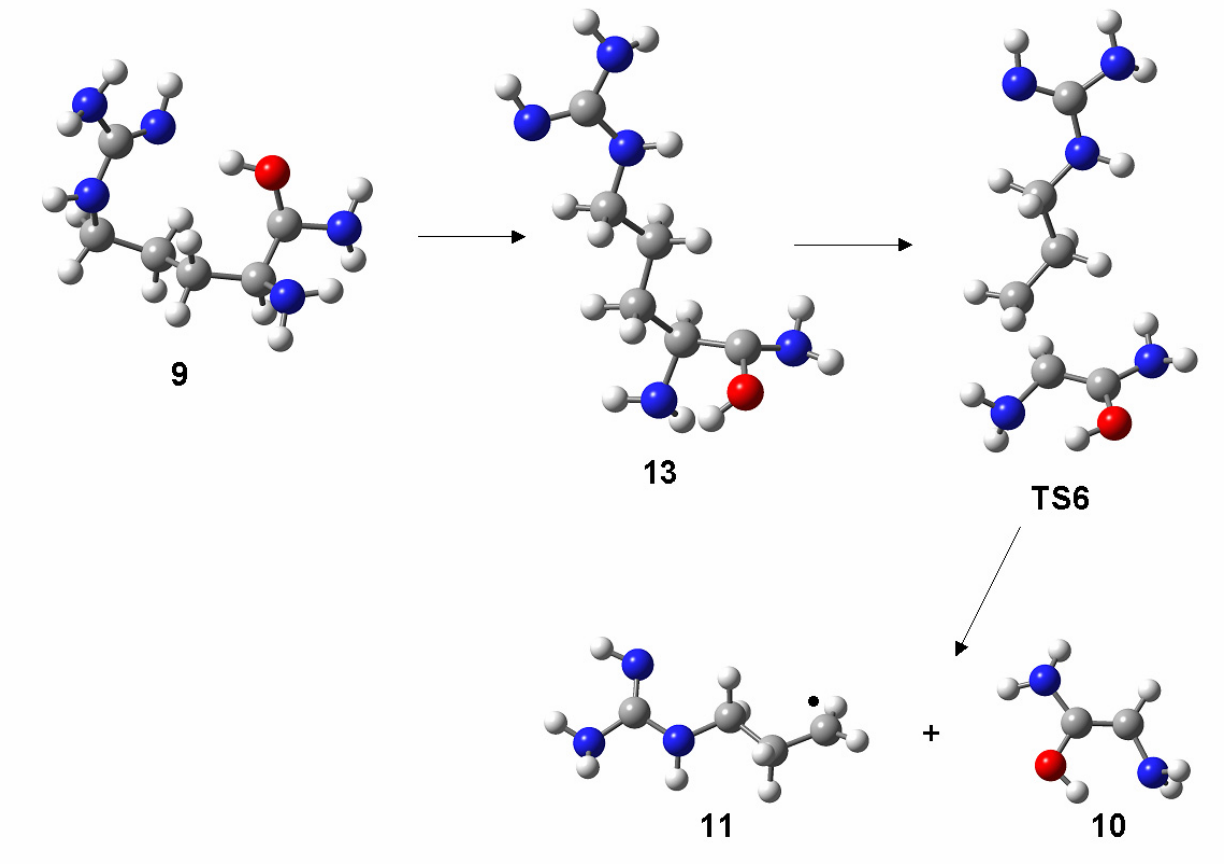


Figure S4. B3LYP/6-31+G(d,p) optimized structure of fragment **12**.



Scheme S1. Dissociation of arginine amide radicals **9** and **13** through **TS6**.