Electronic supplementary information

Pre-Dewar structure modulates protonated azaindole photodynamics

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SI-1. Absorption Spectra

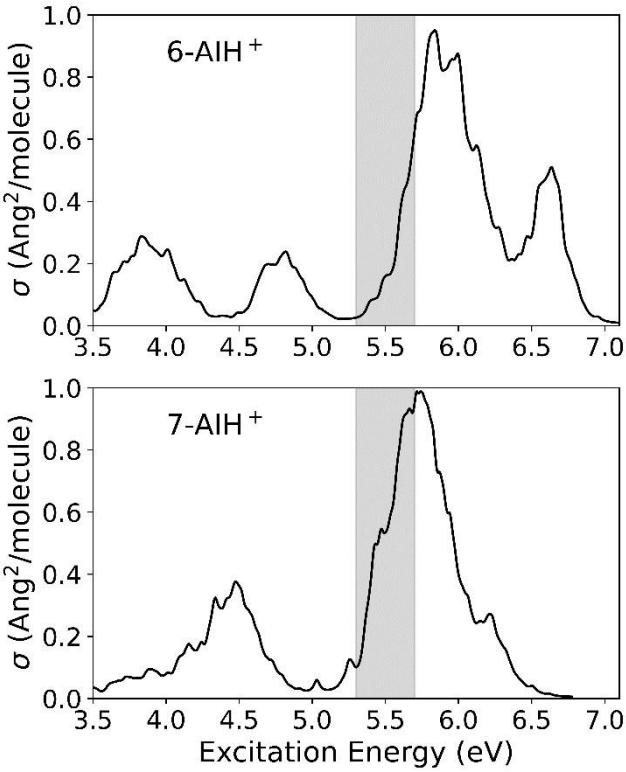


Figure S1. Computed absorption spectra based on 500 points nuclear ensemble for both 6- and 7- protonated azaindole molecules. 60 and 84 initial conditions (geometry and velocity) are sampled from the shaded area under the curve for DC-FSSH dynamics simulations for 6- and 7-protonated azaindole, respectively. ADC(2)/aug-cc-pVDZ.

SI-2. Excitation character of the excited electronic states

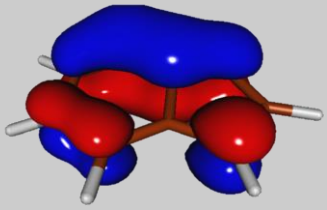
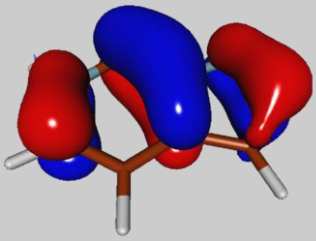
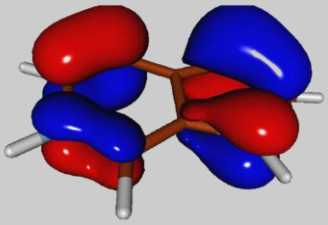
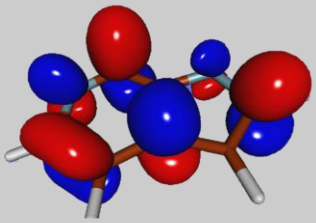
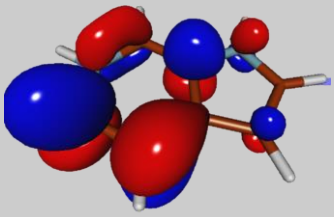
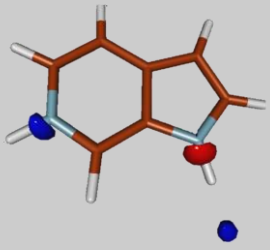
Calculated with ADC(2)/aug-cc-pVDZ.

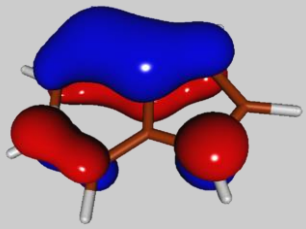
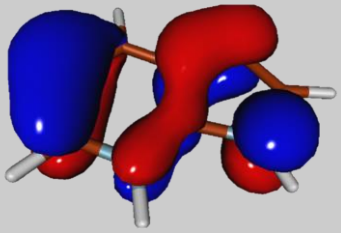
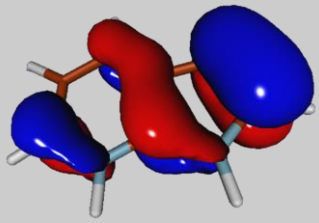
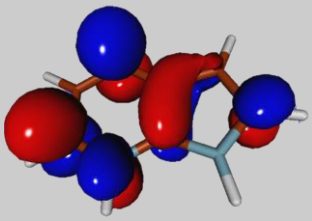
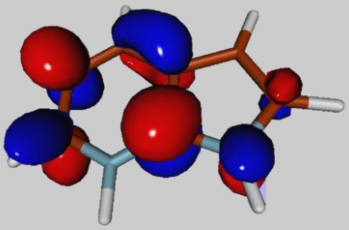
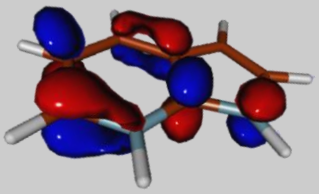
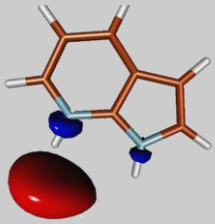
State	ΔE (eV)	Excitation (%)	Character	ΔE (eV)	Excitation (%)	Character
	6-AIH$^+$ S_0 minimum			**7-AIH$^+$ S_0 minimum**		
S_0	0.0			0.0		
S_1	3.95	31 → 32: 85.8	ππ*	3.97	31 → 32: 50.5 30 → 32: 42.1	ππ* ππ*
S_2	5.01	30 → 32: 60.6 31 → 36: 32.5	ππ* ππ*	4.55	30 → 32: 42.8 31 → 32: 37.9	ππ* ππ*
S_3	5.77	31 → 36: 53.5 30 → 32 29.9	ππ* ππ*	5.87	31 → 38: 43.4 31 → 39: 17.5	ππ* ππ*
S_4	6.17	29 → 32: 53.6 30 → 36: 37.3	ππ* ππ*	6.17	31 → 33: 66.0 30 → 33: 13.7	πσ* πσ*
S_5	6.41	31 → 33: 77.1	πσ*	6.40	29 → 32: 37.3 30 → 38: 36.8 30 → 39: 12.7	ππ* ππ* ππ*
S_6	6.74	31 → 34: 68.1	πσ*	6.74	30 → 33: 63.7 31 → 33: 15.6	πσ* πσ*
	6-AIH$^+$ S_1 minimum			**7-AIH$^+$ S_1 minimum**		
S_0	0.34			0.70		
S_1	3.66	31 → 32: 89.0	ππ*	3.45	31 → 32: 85.2	ππ*
S_2	5.17	31 → 36: 48.6 30 → 32: 43.2	ππ* ππ*	4.91	30 → 32: 73.7	ππ*
S_3	5.83	30 → 32: 43.6 31 → 36: 38.9	ππ* ππ*	5.97	31 → 38: 42.3 31 → 39: 20.5	ππ* ππ*
S_4	6.24	29 → 32: 80.6	ππ*	6.34	31 → 33: 75.0	πσ*
S_5	6.44	31 → 33: 74.3	πσ*	6.77	29 → 32: 73.9	ππ*
S_6	6.72	31 → 34: 65.9	πσ*	7.16	31 → 34: 46.0 31 → 35: 11.7	πσ* πσ*

	6-AIH$^+$ S_2 minimum			**7-AIH$^+$ S_2 minimum**		
S_0	0.86			0.41		
S_1	4.48	31 → 32: 63.9 31 → 33: 15.3	ππ* ππ*	4.06	30 → 32: 53.8 31 → 32: 39.9	ππ* ππ*
S_2	4.84	31 → 34: 42.0 31→ 33: 25.7 31→ 32: 21.2	ππ* ππ* ππ*	4.30	31 → 32: 52.8 30 → 32: 37.2	ππ* ππ*
S_3	6.30	30 → 32: 80.5	ππ*	6.14	31 → 38: 36.6 29 → 32: 19.5 31 → 39: 16.9	ππ* ππ* ππ*
S_4	6.51	30 → 34: 34.9 30 → 33: 29.5 29 → 32: 19.9	ππ* ππ* ππ*	6.51	30 → 38: 35.7 29 → 32: 34.2 30 → 39: 13.8	ππ* ππ* ππ*
S_5	6.84	31 → 33: 44.6 31 → 34: 31.2	ππ* ππ*	6.64	31 → 33: 72.2	πσ*
S_6	7.08	31 → 35: 63.0	πσ*	6.95	30 → 33: 65.6	πσ*
	6-AIH$^+$ S_3 minimum			**7-AIH$^+$ S_3 minimum**		
S_0	0.21			0.52		
S_1	3.92	31 → 32: 85.5	ππ*	3.97	31→ 32: 71.8 30→ 32: 22.3	ππ* ππ*
S_2	4.97	31 → 35: 48.8 30 → 32: 41.3	ππ* ππ*	4.76	30 → 32: 47.7 31 → 35: 18.9 31 → 32: 16.4	ππ* ππ* ππ*
S_3	5.55	30 → 32: 48.9 31 → 35: 34.7	ππ* ππ*	5.47	31 → 35: 31.6 30 → 32: 21.3 31 → 33: 14.1	ππ* ππ* πσ*
S_4	6.12	30 → 35: 55.6 29 → 32: 32.8	ππ* ππ*	6.41	30 → 35: 34.9 29 → 32: 24.1 30 → 33: 16.7	ππ* ππ* πσ*
S_5	6.48	31 → 33: 75.7	πσ*	6.57	31 → 33: 57.5	πσ*
S_6	6.78	31 → 34: 66.0	πσ*	6.94	29 → 32: 45.0	ππ*

SI-3. Molecular orbitals

ADC(2)/aug-cc-pVDZ.

6-AIH$^+$ S$_0$ minimum			
MO character	**MOs**		
π	**29**	**30**	**31**
			
π*	**32**	**36**	
			
σ*	**33**	**34**	
			

7-AIH$^+$ S_0 minimum			
MO character	**MOs**		
π	**29**	**30**	**31**
			
π*	**32**	**38**	**39**
			
σ*	**33**		
			

SI-4. Example of density difference plots at few hopping events

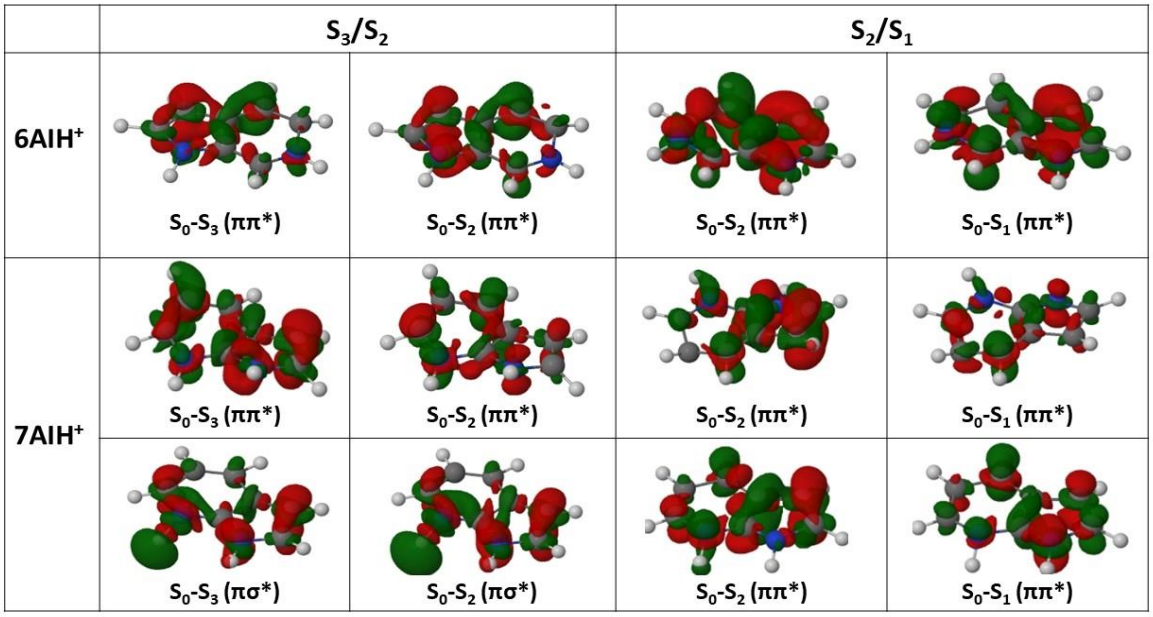


Figure S2. Example of density difference plots at few hopping events. For 6-AIH$^+$, the left plots illustrate an S_3/S_2 hopping with both states having ππ* character. The plots at the right illustrate the density difference at the S_2/S_1 hopping time. Again, both states are ππ*. For 7-AIH$^+$, the top plots at left correspond to an S_3/S_2 hopping involving only ππ* states. The bottom-let plots show an S_3/S_2 hopping between two πσ* states. The plots at right show the density differences for two S_2/S_1 hoppings, only involving ππ* states. The electron is promoted from the red to green region.

SI-5. Simulations with cc-pVDZ basis set

SI-5.1. Excitation energies with cc-pVDZ basis set

Excitation energies (in eV) relative to the minimum of the ground state calculated at ADC(2)/cc-pVDZ level of theory. Oscillator strengths are given in the square brackets.

	6-AIH$^+$				7-AIH$^+$			
	ΔE_0 / eV	ΔE_1 / eV [f_{10}]	ΔE_2 / eV [f_{20}]	ΔE_3 / eV [f_{30}]	ΔE_0 / eV	ΔE_1 / eV [f_{10}]	ΔE_2 / eV [f_{20}]	ΔE_3 / eV [f_{30}]
S_0 min	0.00	4.03 [0.12]	5.12 [0.05]	5.95 [0.48]	0.00	4.09 [0.03]	4.67 [0.17]	6.06 [0.54]
S_1 min	0.35	3.74 [0.11]	5.28 [0.01]	6.00 [0.52]	0.54	3.56 [0.04]	4.99 [0.10]	6.05 [0.52]
S_2 min	0.23	4.11 [0.09]	4.98 [0.16]	6.12 [0.29]	0.29	4.14 [0.03]	4.42 [0.21]	6.21 [0.28]
S_3 min	0.22	4.01 [0.1]	5.08 [0.02]	5.71 [0.44]	0.30	3.86 [0.04]	4.79 [0.08]	5.75 [0.55]

SI-5.2. Adiabatic population with cc-pVDZ basis set

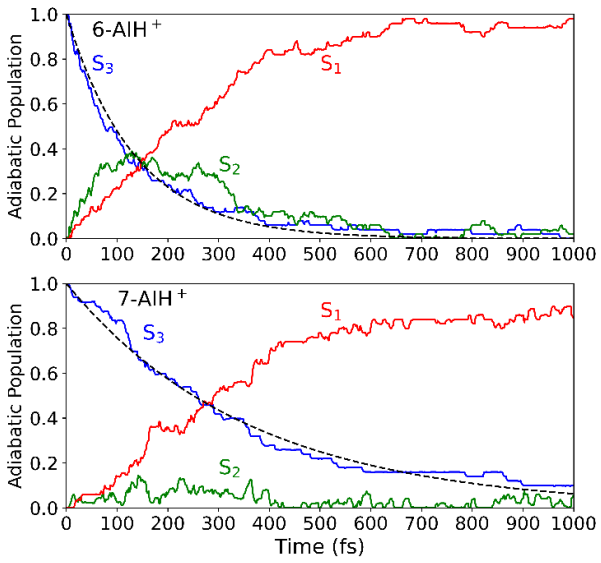


Figure S3. Adiabatic population evolution calculated with ADC(2)/ cc-pVDZ for 6-AIH$^+$ (top) and 7-AIH$^+$ (bottom). The dashed line indicates the S_3 population fitting.

SI-6. Cartesian coordinates of the critical points

6-AIH$^+$ S_0 minimum

C	-2.8325030	-1.2876797	-3.1895658
C	-1.5076657	-0.8139186	-3.4120107
C	-1.6092355	0.6006824	-3.6761947
N	-2.9304925	0.9405032	-3.6113719
C	-3.6736735	-0.1879054	-3.3194323
C	-0.2254367	-1.4081979	-3.4229936
C	0.8760351	-0.6061203	-3.6871014
N	0.7083950	0.7351871	-3.9308870
C	-0.4798277	1.3780631	-3.9385628
H	-4.7558595	-0.1212138	-3.2246744
H	-3.3173047	1.8680471	-3.7550606
H	-0.0776847	-2.4720800	-3.2312949
H	-3.1448824	-2.3042003	-2.9629405
H	-0.4764876	2.4482068	-4.1468148
H	1.9014925	-0.9710571	-3.7179086
H	1.5441762	1.2873982	-4.1203524

6-AIH$^+$ S_1 minimum

C	-2.8489336	-1.2851520	-3.1836059
C	-1.4861016	-0.7887454	-3.4177230
C	-1.5922979	0.5757543	-3.6766713
N	-2.9592191	0.9017222	-3.6040149
C	-3.7355308	-0.1719565	-3.3150209
C	-0.2043872	-1.4229862	-3.4198552
C	0.8926680	-0.6018112	-3.6880431
N	0.7523495	0.7336293	-3.9366674
C	-0.4817381	1.4196042	-3.9542596
H	-4.8166862	-0.1002360	-3.2217203
H	-3.3291645	1.8432908	-3.7514345
H	-0.0625424	-2.4856471	-3.2256951
H	-3.1490731	-2.3072370	-2.9512020
H	-0.4882527	2.4861597	-4.1668327
H	1.9140836	-0.9835804	-3.7126005
H	1.5938715	1.2729058	-4.1218198

6-AIH$^+$ S_2 minimum

C	-2.8466149	-1.2842201	-3.2431518
C	-1.4469907	-0.8132218	-3.3089470
C	-1.5510959	0.6212143	-3.4683149
N	-2.9595214	0.9562686	-3.4983699
C	-3.6953691	-0.1527491	-3.3430462
C	-0.2384487	-1.4408655	-3.3580282
C	0.9504738	-0.5409970	-3.5009630
N	0.7165975	0.7152592	-4.0010444
C	-0.4870838	1.3555722	-4.0028000
H	-4.7844237	-0.1155345	-3.3077630
H	-3.3390778	1.9015806	-3.5211669
H	-0.1073000	-2.5241123	-3.3577182

H	-3.1908120	-2.3170830	-3.1735473
H	-0.5239785	2.3682263	-4.4037591
H	1.9820070	-0.8910919	-3.5192049
H	1.5206838	1.2474688	-4.3393416

6-AIH$^+$ S_3 minimum

C	-2.8576938	-1.2929415	-3.1837344
C	-1.4796781	-0.8308111	-3.4108110
C	-1.5966410	0.5778427	-3.6747259
N	-2.9560693	0.9400326	-3.6116032
C	-3.7056202	-0.1814555	-3.3184925
C	-0.2185339	-1.4413885	-3.4138284
C	0.9062983	-0.6207003	-3.6832074
N	0.7262233	0.7641609	-3.9397881
C	-0.4581570	1.4104356	-3.9510142
H	-4.7898703	-0.1229953	-3.2236258
H	-3.3326126	1.8737570	-3.7599274
H	-0.0748294	-2.5051861	-3.2192344
H	-3.1851727	-2.3063694	-2.9509818
H	-0.4802973	2.4804288	-4.1602208
H	1.9369144	-0.9702142	-3.7130513
H	1.5647852	1.3111189	-4.1329197

6-AIH$^+$ S_3/S_2 CI

C	-1.74361624	-1.26927925	0.22051679
C	-0.19671734	-0.72895579	0.29991322
C	-0.33444245	0.50815126	-0.39780164
N	-1.64553089	0.98903934	-0.14130446
C	-2.48906004	-0.15704933	0.04348100
C	1.11829860	-1.36624762	0.26596597
C	2.18377320	-0.56885144	0.06865713
N	1.97592304	0.91557860	-0.04867342
C	0.83187201	1.46998799	-0.31497796
H	-3.57330442	-0.04214747	0.06690504
H	-2.00048996	1.84066805	-0.58292656
H	1.25910880	-2.44751279	0.34441367
H	-2.04923145	-2.30928703	0.09924821
H	0.69671015	2.55144430	-0.20222688
H	3.22333643	-0.88360861	-0.00719210
H	2.78960060	1.50960051	0.11166211

6-AIH$^+$ S_2/S_1 CI

C	-1.59102520	-1.23843653	0.30909719
C	-0.19187944	-0.80278716	0.08455352
C	-0.30522557	0.59326530	-0.29205321
N	-1.72146691	0.94527806	-0.24661189
C	-2.44257885	-0.13246304	0.06421389
C	1.01770710	-1.38358774	0.27143293
C	2.20757439	-0.48565856	-0.04757798
N	1.97751779	0.85878823	0.06066894
C	0.76766830	1.46174502	-0.07659367
H	-3.53155412	-0.09766140	0.10578064

H	-2.10966077	1.84423644	-0.52700951
H	1.17730264	-2.36398087	0.72089129
H	-1.93143245	-2.22336502	0.63479564
H	0.73172768	2.55037080	-0.03411828
H	3.24416699	-0.81115491	0.05070896
H	2.78776840	1.47351122	0.16415156

7-AIH$^+$ S_0 minimum

C	0.4888818	-1.4644741	0.4850103
C	0.6693387	-1.8269520	1.8096029
H	1.3118322	-2.5875639	2.2480058
C	-0.4759151	-0.4036677	0.4776439
N	-0.1377265	-1.0423101	2.6325793
C	-0.8352043	-0.1792812	1.8457720
C	-1.0886876	0.3921746	-0.5089338
H	-0.8469850	0.2593185	-1.5659174
N	-1.7386112	0.7672168	2.1935847
C	-2.0197678	1.3626938	-0.1065521
H	-2.5182849	2.0000072	-0.8376385
C	-2.3361304	1.5395670	1.2464869
H	-3.0520673	2.2765942	1.6087803
H	0.9886634	-1.9081632	-0.3720380
H	-1.9856883	0.9150653	3.1725924
H	-0.1824473	-1.1199362	3.6437751

7-AIH$^+$ S_1 minimum

C	-0.5635977	-1.4702295	0.9892289
C	-0.3086395	-1.8363062	2.3664221
H	0.3547788	-2.5953920	2.7779674
C	-1.5497584	-0.4106532	0.9815380
N	-1.0737070	-1.0554892	3.1216782
C	-1.8600686	-0.1812232	2.3035349
C	-2.1504597	0.3887727	-0.0734049
H	-1.9423908	0.2145217	-1.1293426
N	-2.6722445	0.8300373	2.7644394
C	-3.0294388	1.3907791	0.3919132
H	-3.5363127	2.0493889	-0.3171316
C	-3.3051367	1.5967128	1.7453151
H	-3.9853084	2.3685152	2.1056746
H	-0.0779604	-1.9310804	0.1272540
H	-3.1519232	0.7415941	3.6588422
H	-1.0931792	-1.0835344	4.1429696

7-AIH$^+$ S_2 minimum

C	1.7709252	-1.4100170	1.6780814
C	1.9656951	-1.8004870	2.9985951
H	2.6648152	-2.4962021	3.4570302
C	0.6935090	-0.4815930	1.6535971
N	1.0190299	-1.1032894	3.8055882
C	0.2593317	-0.3334196	3.0099109
C	0.0596614	0.3052055	0.5842527
H	0.3529090	0.2215527	-0.4614081
N	-0.7453928	0.5711306	3.4316485

C	-0.9487258	1.1759472	1.0415845
H	-1.4865147	1.8283890	0.3506039
C	-1.3597824	1.2575491	2.4174546
H	-2.1917851	1.8998308	2.7142562
H	2.3439754	-1.7680219	0.8253939
H	-1.2361535	0.4359422	4.3156833
H	0.9613547	-1.1700924	4.8199953

7-AIH$^+$ S_3 minimum

C	1.2900211	-1.5022083	0.9638777
C	1.4566099	-1.9255084	2.3010451
H	2.0062087	-2.7834658	2.6886077
C	0.4666986	-0.2941356	0.9775907
N	0.7772559	-1.0768489	3.1389126
C	0.1953137	-0.0187850	2.3629591
C	-0.1915096	0.4694967	-0.0370958
H	0.0763861	0.3655842	-1.0917279
N	-0.9605925	0.6599905	2.7119394
C	-1.1880582	1.3553298	0.3800618
H	-1.7030343	2.0101170	-0.3248672
C	-1.6399030	1.3537610	1.7520244
H	-2.4973250	1.9352321	2.0940870
H	1.6640246	-2.0344878	0.0888643
H	-1.2576637	0.7259206	3.6881450
H	0.9353091	-1.0346944	4.1447611

7-AIH$^+$ S_3/S_2 CI

C	1.7809510	-1.4246346	1.6675230
C	1.9636957	-1.8429458	2.9738613
H	2.6567643	-2.5474976	3.4308018
C	0.6970134	-0.5155636	1.6513658
N	0.9920472	-1.1615371	3.8004208
C	0.2477012	-0.3939050	3.0148175
C	0.0580664	0.2849993	0.5827028
H	0.3629080	0.2168981	-0.4603533
N	-0.7667063	0.5179907	3.4380169
C	-0.9360304	1.1582902	1.0502962
H	-1.4652873	1.8315105	0.3733427
C	-1.3505354	1.2243057	2.4339784
H	-2.1700583	1.8863102	2.7277574
H	2.3670355	-1.7572879	0.8120656
H	-1.2362202	0.4116116	4.3351140
H	0.9215253	-1.2561146	4.8105392

7-AIH$^+$ S_2/S_1 CI

C	1.6518116	-1.3951096	1.6742133
C	1.5731644	-1.9715865	2.9395709
H	1.8274883	-2.9918227	3.2383435
C	1.1532008	0.0408397	1.7886489
N	1.1552129	-1.0564690	3.8436954
C	0.7693253	0.2161721	3.1711839
C	0.2987791	0.6205816	0.7114972
H	0.7124981	0.7245821	-0.2959969

N	-0.6271904	0.6007932	3.3860832
C	-0.9884995	0.9130600	1.0113838
H	-1.6905842	1.2502214	0.2374918
C	-1.4500749	0.8706977	2.3607182
H	-2.4911634	1.0841741	2.6267657
H	1.9471898	-1.8936651	0.7525491
H	-0.9274818	0.7752598	4.3381214
H	1.2091949	-1.1552982	4.8579793

SI-7. Puckering analysis

The Cremer-Pople puckering[3] analysis of all points in S_3 during the dynamics is shown in Figure S4. For 6-AIH$^+$, the trajectories span the entire θ–ϕ space uniformly. Such a distribution is expected for a molecule with a planar minimum in S_3. In the case of 7-AIH$^+$, the trajectories cluster around the ϕ = 45°, θ = 90º region, in which S_3 has a minimum (ϕ = 50°, θ = 78º) with a C5-C7a boat conformation.[4]

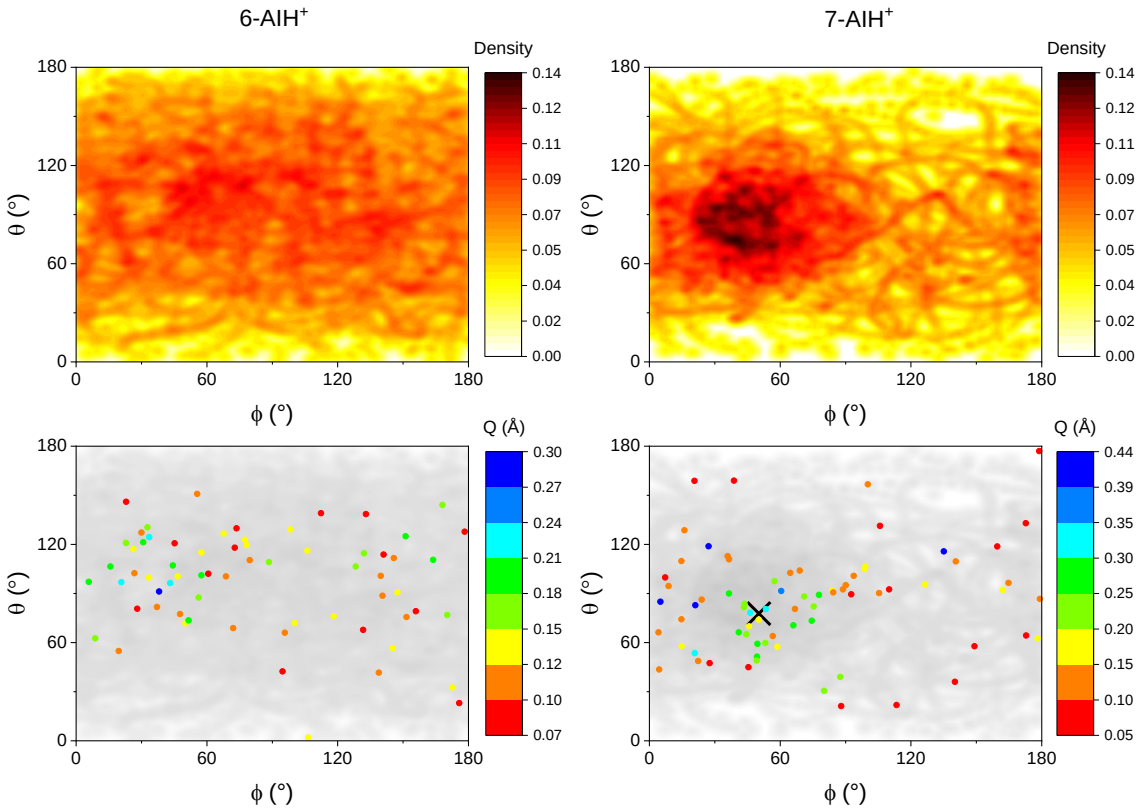


Figure S4. Cremer-Pople puckering analysis of all points in the S_3 state during the dynamics of 6-AIH$^+$ (left) and 7-AIH$^+$ (right) (ADC(2)/aug-cc-pVDZ). The figures at the top are heat maps, with the dark regions indicating that more points are located there. The figure at the bottom shows the hopping points (dots) colored by the puckering degree Q. The same density from the top figures is also shown in the bottom in gray. The cross in 7-AIH$^+$ indicates the S_3 minimum (Q = 0.18 Å). The planar minimum of 6-AIH$^+$ does not appear in this type of graph. All graphs show only points with Q > 0.04 Å.

	<Q> / Å (Q > 0.04 Å)	<Q> / Å (Q > 0 Å)
6-AIH$^+$	0.14	0.11
7-AIH$^+$	0.20	0.19

The mean value of Q in S_3 is shown in the table above. The algorithm we use computes Q only if it is bigger than 0.04 Å.[5] The mean values of 0.14 Å for 6-AIH$^+$ and 0.20 Å for 7-AIH$^+$ imply that 7-AIH$^+$ dynamics are significantly more puckered than 6-AIH$^+$ dynamics. The contrast is even stronger if we consider the near planar points with Q < 0.04 Å. Because they are proportionally more numerous in 6-AIH$^+$ (22% of the total) than in 7-AIH$^+$ (8%), the deviation between the Q mean values tends to be more significant. If we attribute uniform random values between 0 and 0.04 Å for the near planar points, the mean values are 0.11 and 0.19 Å for 6-AIH$^+$ and 7-AIH$^+$, respectively.

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