

Supplementary Material

Effects of the second hydration shell on excited-state multiple proton transfer: Dynamics simulations of 7-azaindole:(H₂O)₁₋₅ clusters in the gas phase

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Table S1. Relative energy of three different ground-state isomers of 7Al(H₂O)₃ optimized at RI-ADC(2)/SVP-SV(P) level: bridged-planar, cyclic-nonplanar (2+1), and bicyclic-nonplanar.

Isomer	Energy (kcal.mol ⁻¹)		
	ADC(2) Present result	MP2/cc-pVDZ (B3LYP/cc-pVDZ) by Yu et al. (2012)	CC2/cc-pVDZ (B3LYP/cc-pVDZ) by Pino et al. (2011)
Bridged-planar	0.00	0.00 (0.00)	0.00 (0.00)
Cyclic-nonplanar	-1.57	-0.93 (-0.86)	-
Bicyclic-nonplanar	0.82	0.14 (1.90)	-1.33 (-2.91)

Table S2. Bond distances comparison between SVP-SV(P) and TZVPP basis sets for the ground state structure of the 7Al(H₂O)₃-bridged-planar cluster.

	Distance (Å)	
	SVP-SV(P)	TZVPP
H1-O1	1.74	1.78
H2-O3	1.71	1.73
H3-O2	1.73	1.75
N2-H4	1.80	1.80

Table S3. Average time lag between PTs during dynamics simulation.

Complex	Time (fs)					
	PT1	Time lag	PT2	Time lag	PT3	Time lag
7Al(H ₂ O) ₁	48	10	59			
7Al(H ₂ O) ₁₊₁	91	5	96			
7Al(H ₂ O) ₂	69	1	70	8	78	
7Al(H ₂ O) ₃ bridged-planar	69	4	73	6	79	11
7Al(H ₂ O) ₃ cyclic-nonplanar	77	12	91	8	99	
7Al(H ₂ O) ₃ bicyclic-nonplanar	70	35	105	10	115	
7Al(H ₂ O) ₄	74	9	83	12	95	
7Al(H ₂ O) ₅	74	11	85	26	111	

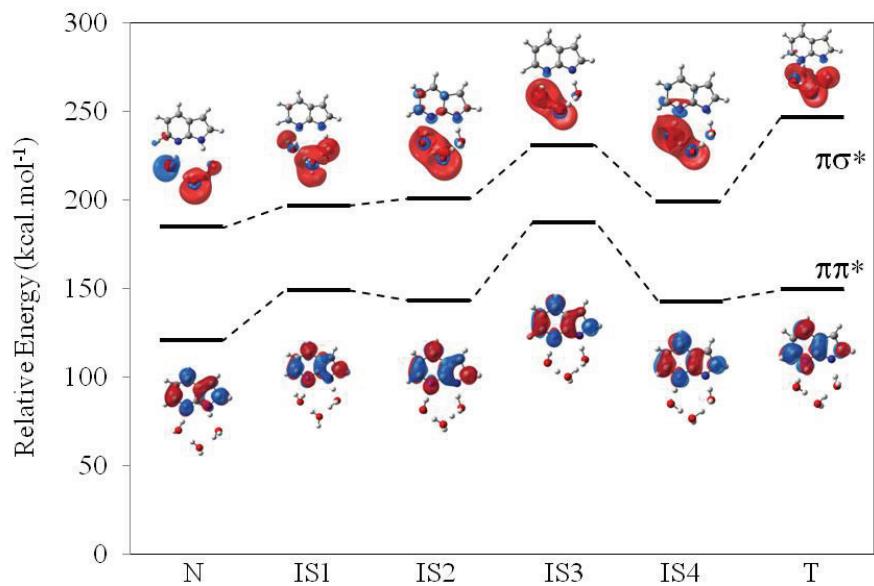


Figure S1. Relative single-point energies at RI-ADC(2)/SVP-SV(P) of first excited states ($\pi\pi^*$ and $\pi\sigma^*$) of a selected trajectory for the 7Al(H_2O)₃-bridged-planar complex.

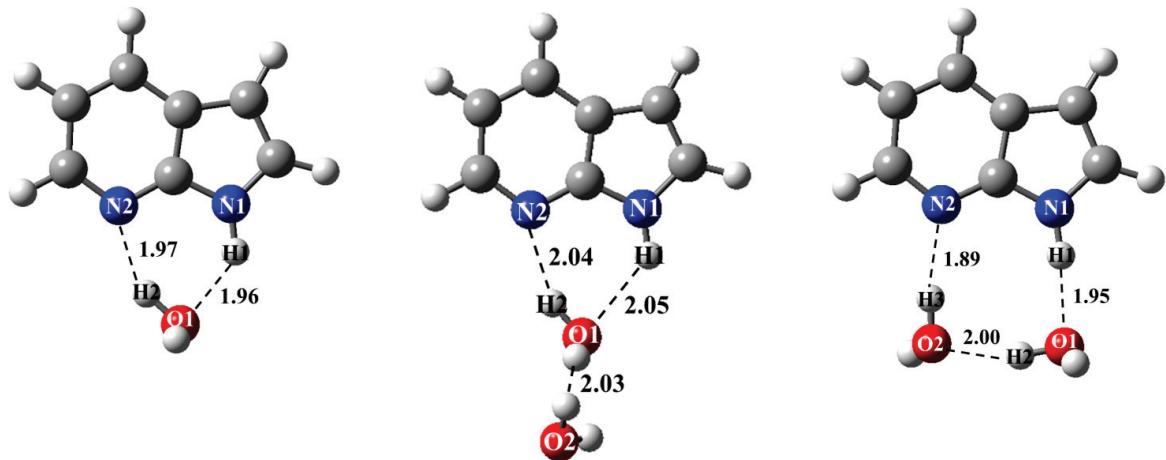


Figure S2. Ground-state structures of 7Al(H₂O)₁, 7Al(H₂O)₁₊₁, and 7Al(H₂O)₂ optimized at ADC(2)/SVP-SV(P).

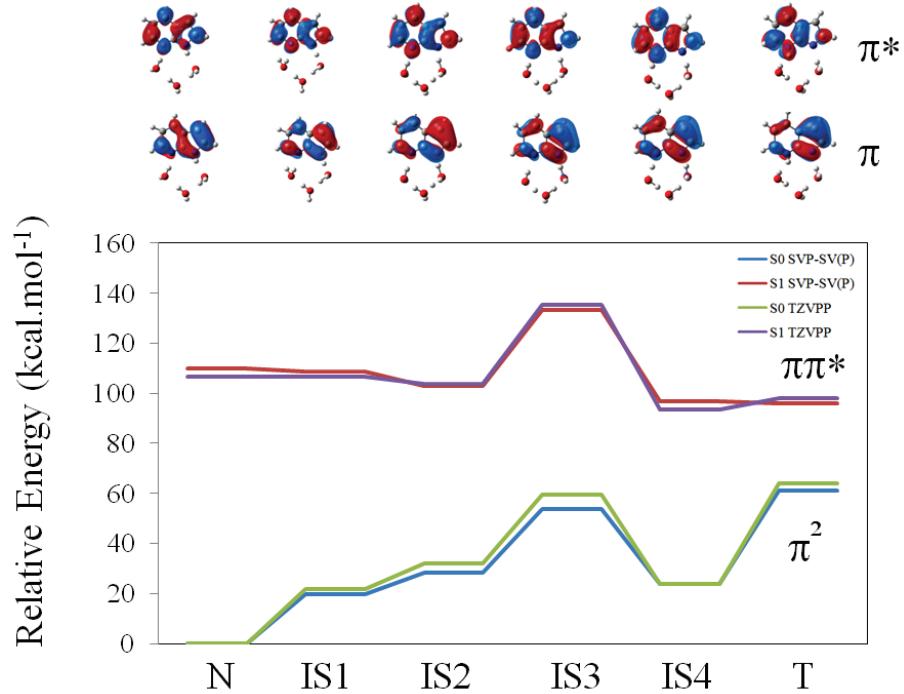


Figure S3. Comparison of relative single-point energies at RI-ADC(2)/SVP-SV(P) and RI-ADC(2)/TZVPP of the ground and first excited states (S_0 and $\pi\pi^*$) of a selected trajectory for the 7Al(H₂O)₃-bridged-planar complex.

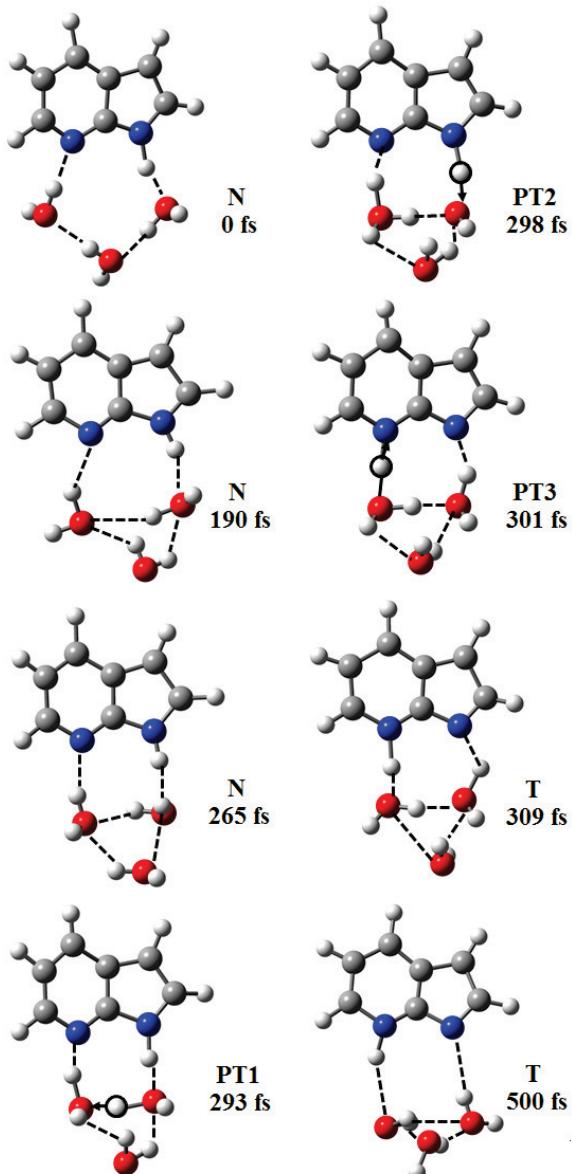


Figure S4. Snapshots of one trajectory of the 7Al(H₂O)₃-bridged-planar dynamics showing the HBR in waters leading it to form 7Al(H₂O)₃-cyclyclic-nonplanar isomer following by triple PT at 500 fs. Normal (N), Proton transfer (PT), and Tautomer (T).

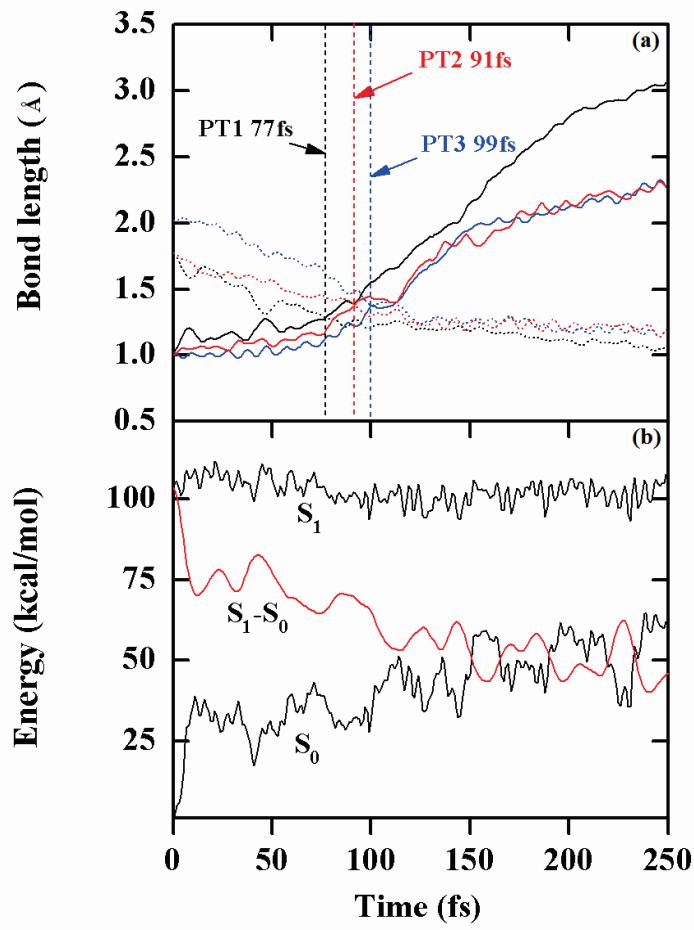


Figure S5. Average values over 19 trajectories of a 7Al(H₂O)₃ cyclic-nonplanar (2+1) isomer complex. (a) Average breaking and forming of bonds showing time evolution. NH1 and O1 $\cdot\cdot$ H1 in black, O4H2 and O2 $\cdot\cdot$ H2 in red, and O2-H3 and N2 $\cdot\cdot$ H3 in blue (b) Average relative energies of excited state (S₁), ground state (S₀), and energy difference of S₁ and S₀ state (S₁-S₂).

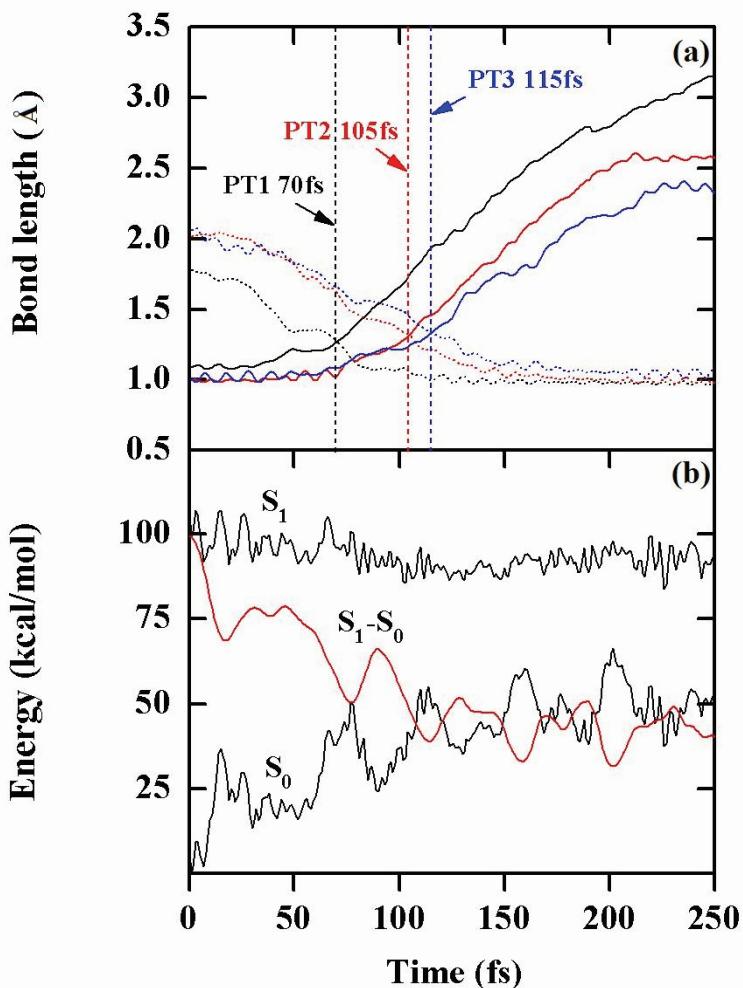


Figure S6. Average values over 30 trajectories of a $7\text{Al}(\text{H}_2\text{O})_3$ bicyclic-nonplanar isomer complex. (a) Average breaking and forming of bonds showing time evolution HN and O1 \cdots H1 in black, O4H2 and O2 \cdots H2 in red, and O2-H3 and N2 \cdots H3 in blue (b) Average relative energies of excited state (S_1), ground state (S_0), and energy difference of S_1 and S_0 state ($S_1 - S_0$).

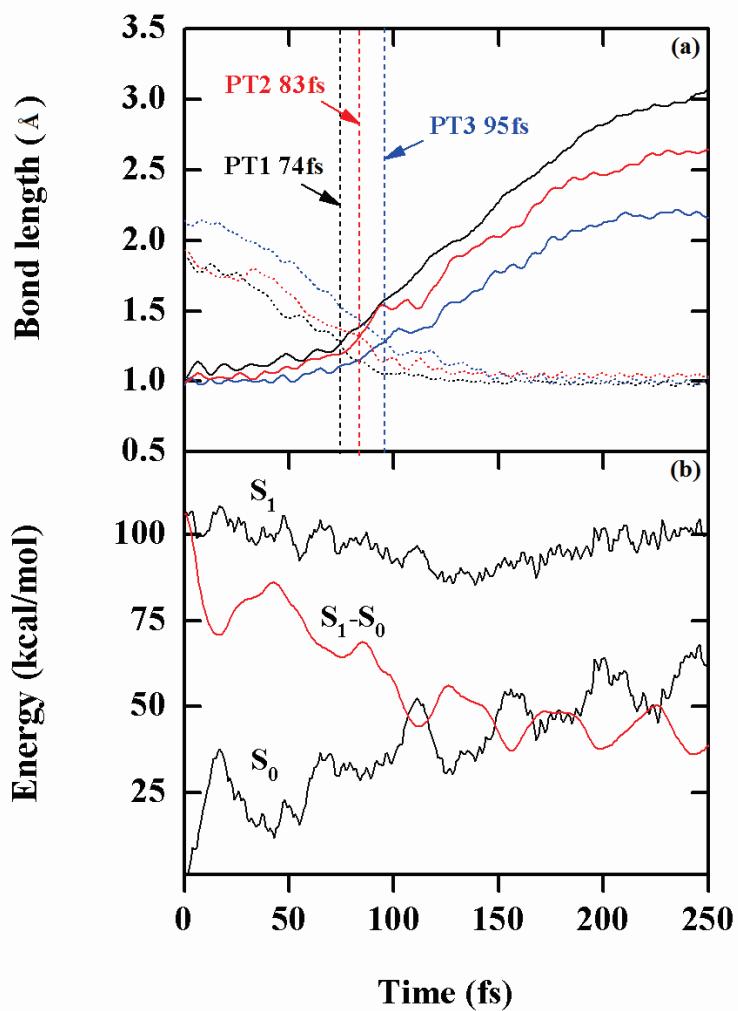


Figure S7. Average values over 40 trajectories of a $7\text{Al}(\text{H}_2\text{O})_4$ complex. (a) Average breaking and forming of bonds showing time evolution. N1-H1 and O1 $\cdot\cdot$ H1 in black, O1-H2 and O2 $\cdot\cdot$ H2 in red, and O2H3 and N2 $\cdot\cdot$ H3 in blue (b) Average relative energies of excited states (S₁), ground state (S₀), and energy difference of S₁ and S₀ state (S₁-S₂).

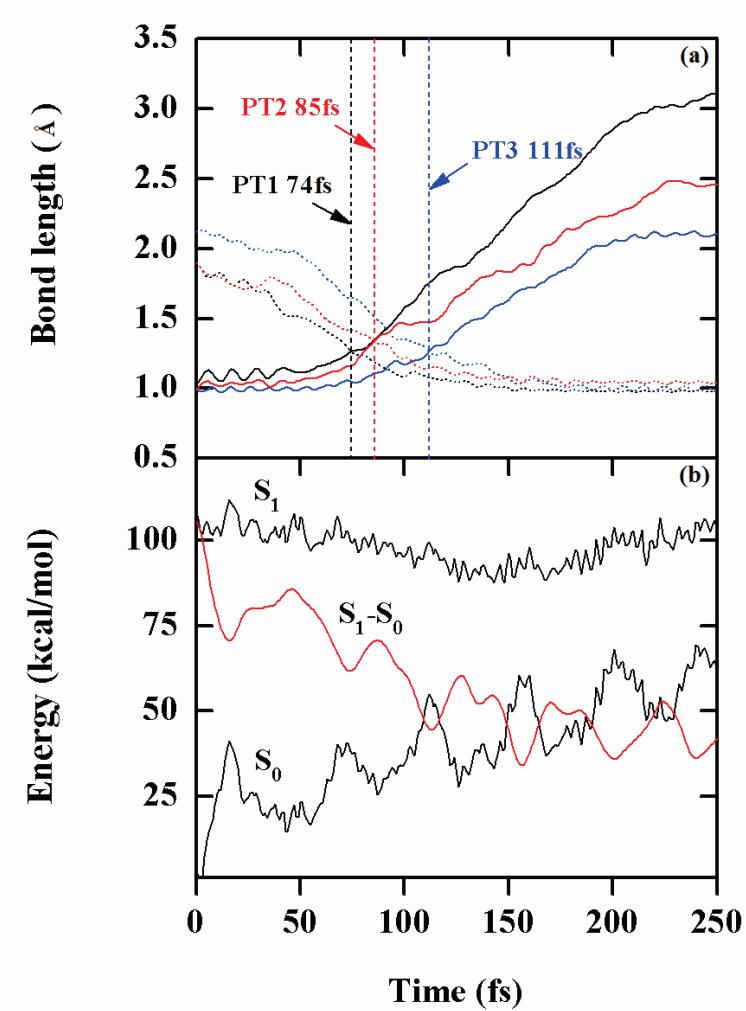


Figure S8. Average values over 38 trajectories of a 7Al(H₂O)₅ complex. (a) Average breaking and forming of bonds showing time evolution.-H1···N1 and O1···H1 in black, O1-H2 and O2···H2 in red, and O2H3 and N2···H3 in blue (b) Average relative energies of excited stated state (S₁), ground state (S₀), and energy difference of S₁ and S₂ state (S₁-S₂).

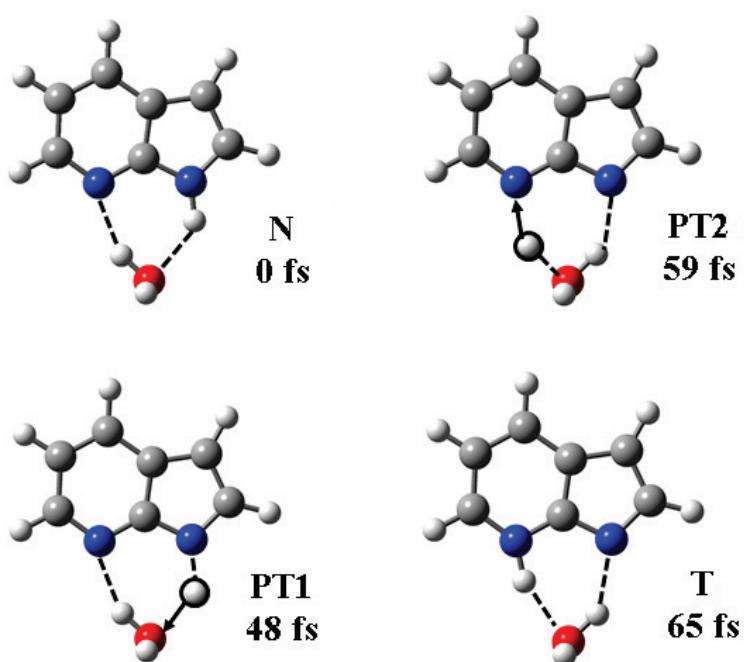


Figure S9. Snapshots representing the average over 12 trajectories of a 7Al(H₂O)₁ complex showing the time evolution of the ESTPT reaction through a hydrogen bonded network within 83 fs. Normal (N), proton transfer (PT), and tautomer (T).

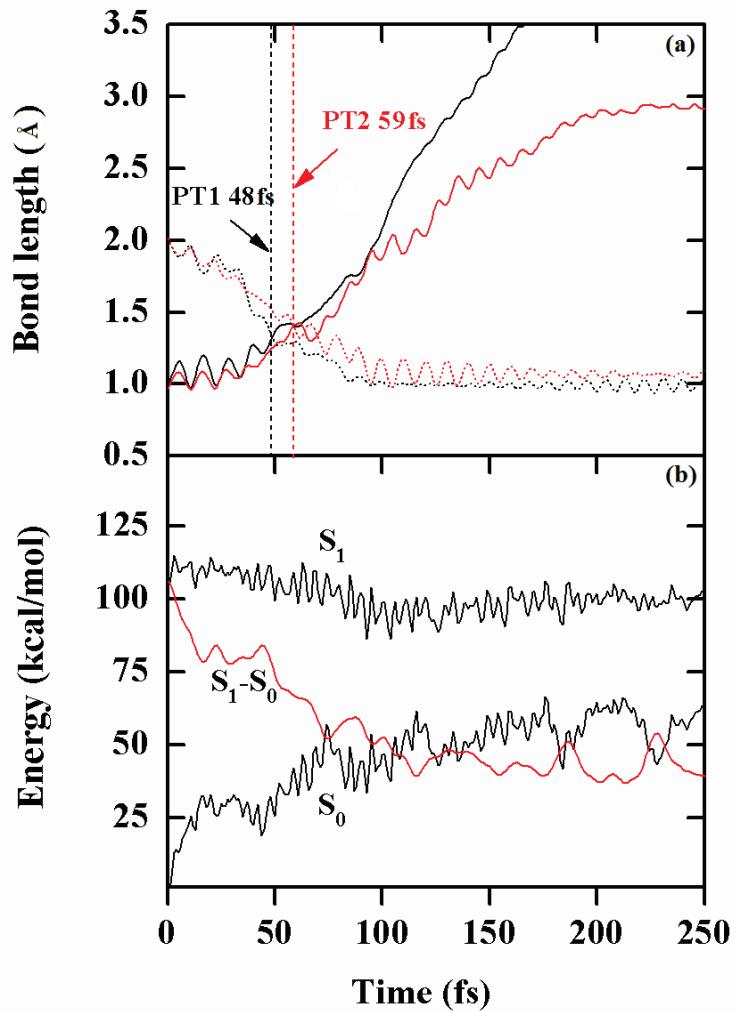


Figure S10. Average values over 12 trajectories of a 7Al(H₂O)₁ complex. (a) Average breaking and forming of bonds showing time evolution. NH1 and O1 $\cdot\cdot$ H1 in black, and O1-H2 and N2 $\cdot\cdot$ H2 in red (b) Average relative energies of excited state (S₁), ground state (S₀), and energy difference of S₁ and S₀ state (S₁-S₀).

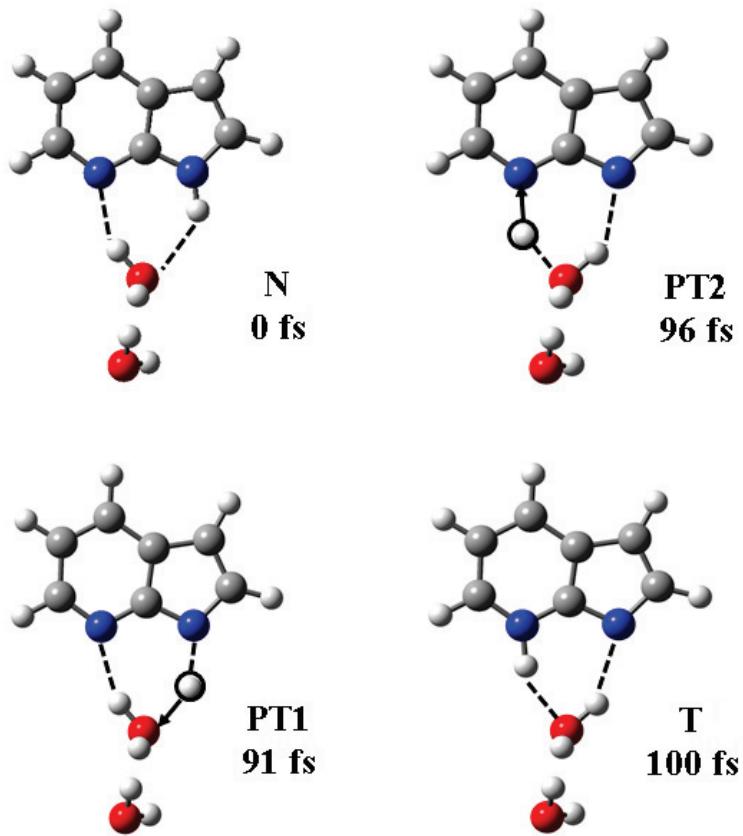


Figure S11. Snapshots representing the average over 18 trajectories of a $7\text{Al}(\text{H}_2\text{O})_{1+1}$ complex showing the time evolution of the ESTPT reaction through a hydrogen bonded network within 83 fs. Normal (N), proton transfer (PT), and tautomer (T).

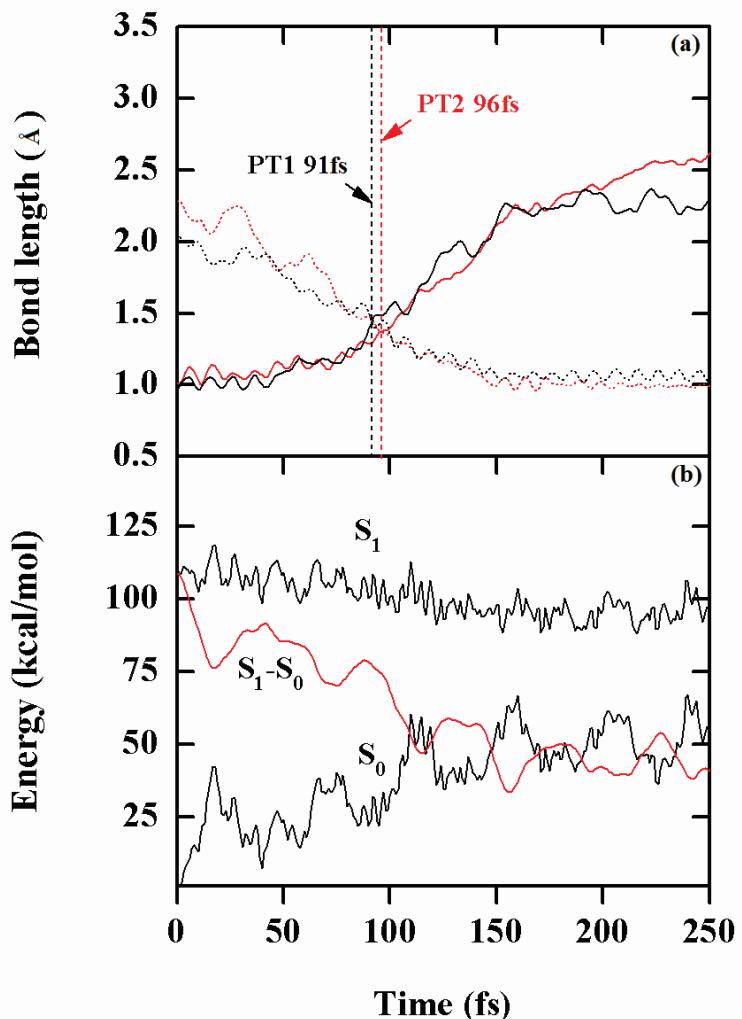


Figure S12. Average values over 18 trajectories of a 7Al(H₂O)₁₊₁ complex. (a) Average breaking and forming of bonds showing time evolution. NH1 and O1···H1 in black, and O1-H2 and N2···H2 in red (b) Average relative energies of excited state (S_1), ground state (S_0), and energy difference of S_1 and S_0 state ($S_1 - S_0$).

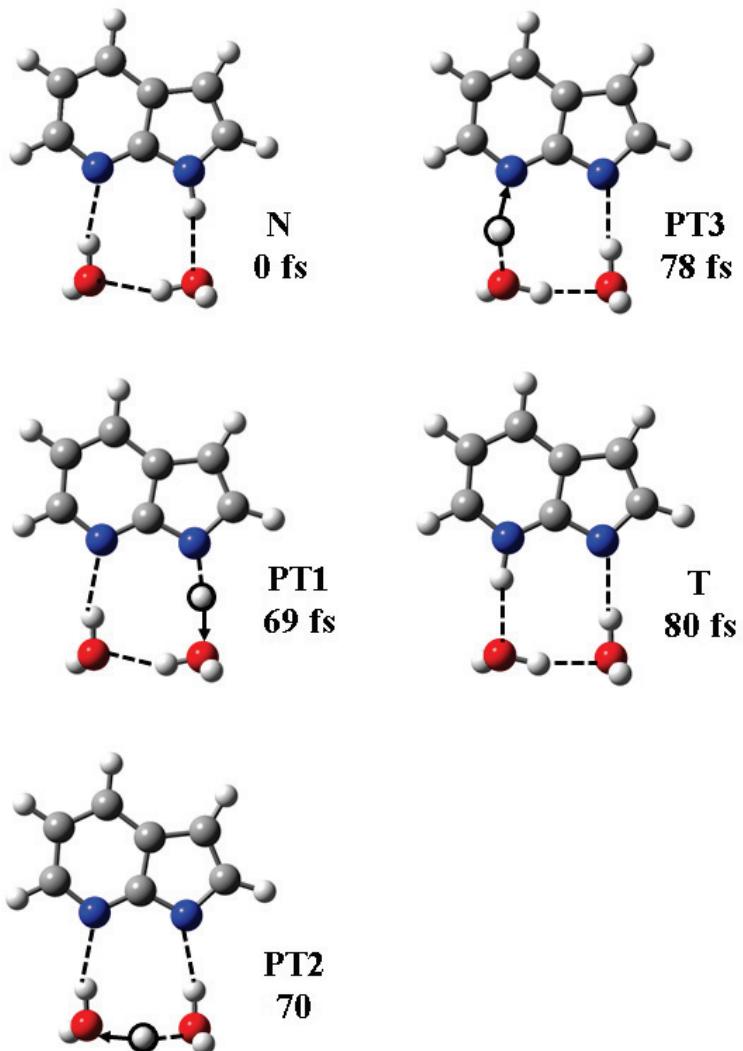


Figure S13. Snapshots representing the average over 20 trajectories of a 7Al(H₂O)₂ complex showing the time evolution of the ESTPT reaction through a hydrogen bonded network within 83 fs. Normal (N), proton transfer (PT), and tautomer (T).

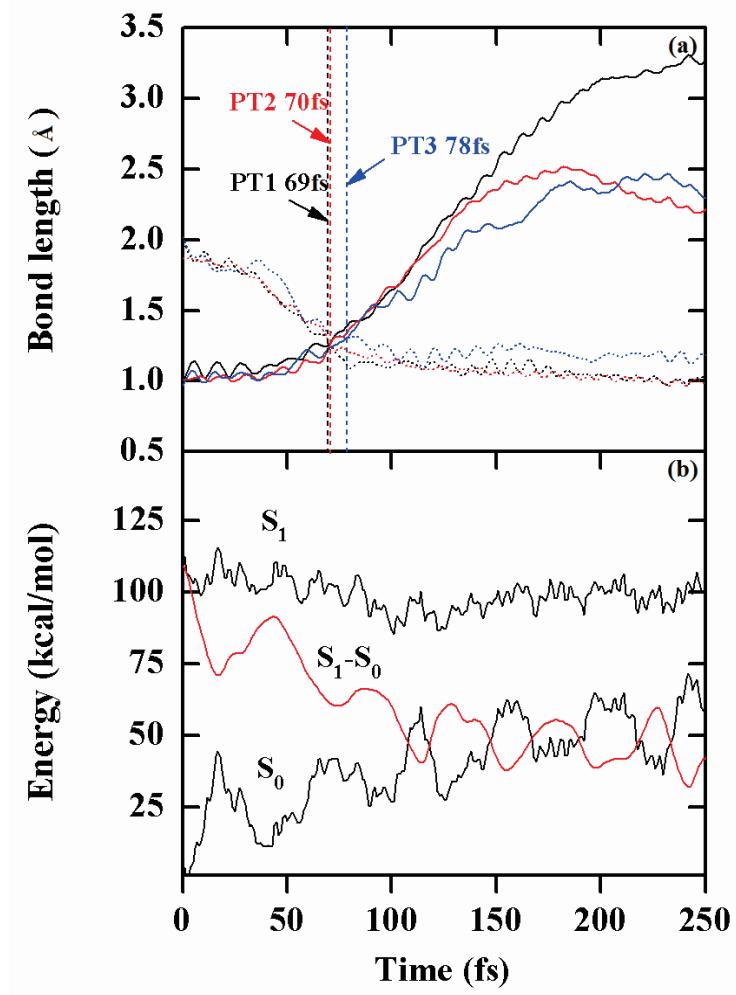


Figure S14. Average values over 20 trajectories of a $7\text{Al}(\text{H}_2\text{O})_2$ complex. (a) Average breaking and forming of bonds showing time evolution.-H11 and O1-H1 in black, O1-H2 and O2-H2 in red, and O2-H3 and N2-H3 in blue (b) Average relative energies of excited state (S_1), ground state (S_0), and energy difference of S_1 and S_0 state ($S_1 - S_0$).

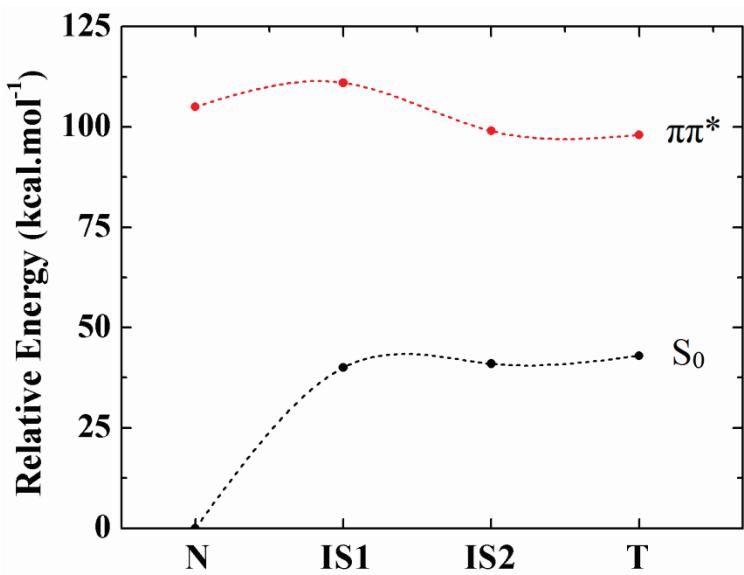


Figure S15. Average relative energies (kcal.mol⁻¹) of the ground (S_0) and the excited states ($\pi\pi^*$) of 7Al(H₂O)₁.

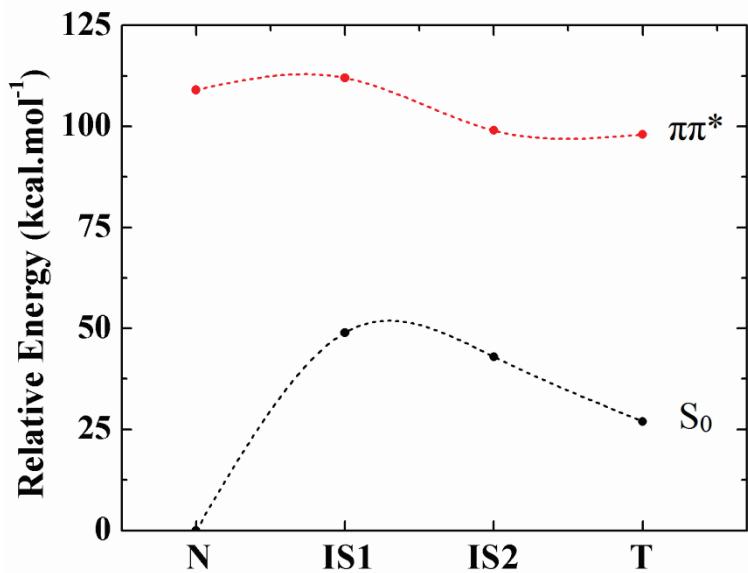


Figure S16. Average relative energies (kcal.mol⁻¹) of the ground (S_0) and the excited states ($\pi\pi^*$) of 7Al(H₂O)₁₊₁.

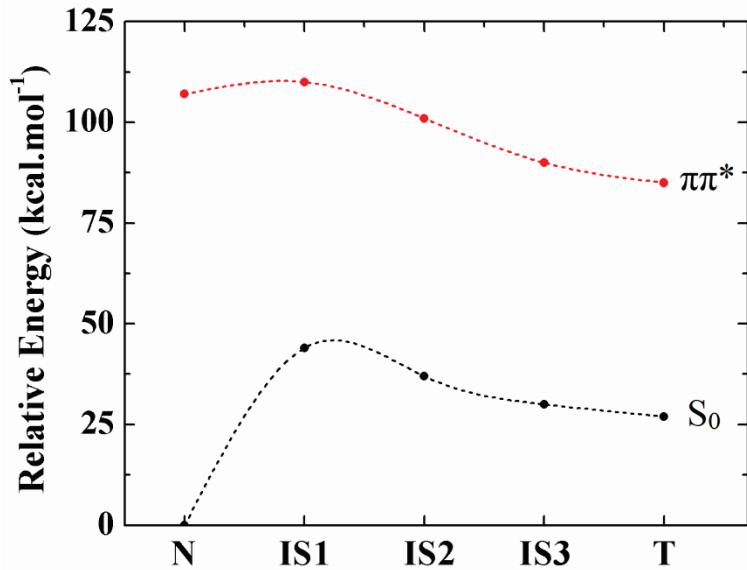


Figure S17. Average relative energies ($\text{kcal} \cdot \text{mol}^{-1}$) of the ground (S_0) and the excited states ($\pi\pi^*$) of $7\text{Al}(\text{H}_2\text{O})_2$.

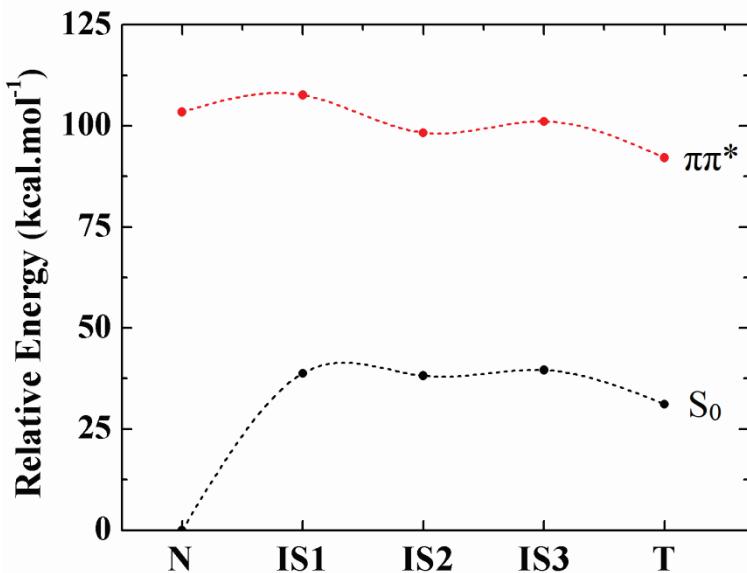


Figure S18. Average relative energies ($\text{kcal} \cdot \text{mol}^{-1}$) of the ground (S_0) and the excited states ($\pi\pi^*$) of $7\text{Al}(\text{H}_2\text{O})_3$ -cyclic-nonplanar (2+1) isomer.

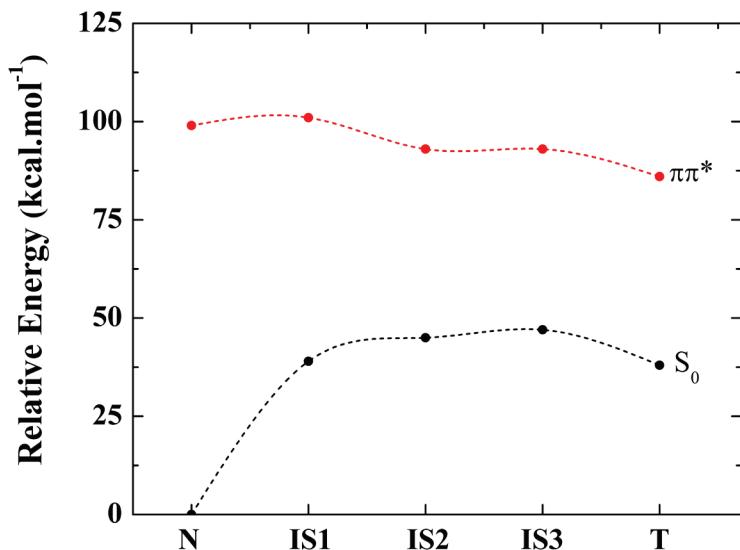


Figure S19. Average relative energies (kcal.mol⁻¹) of the ground (S_0) and the excited states ($\pi\pi^*$) of 7Al(H₂O)₃-bicyclic-nonplanar isomer.

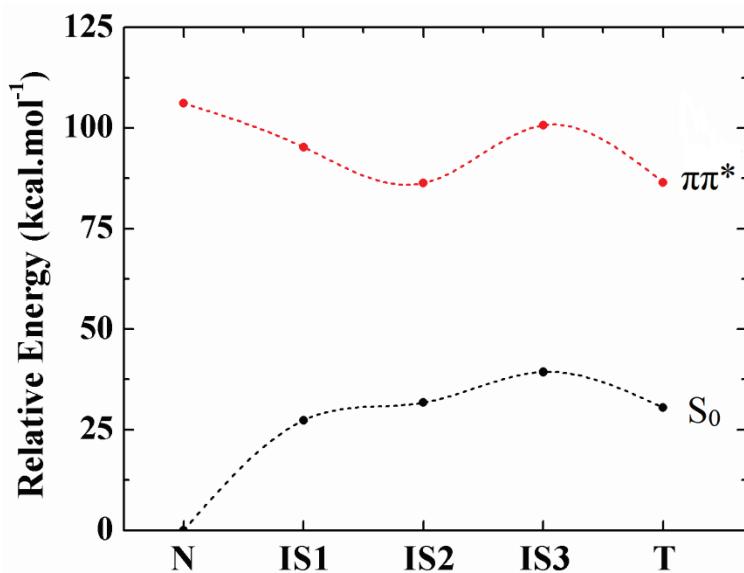


Figure S20. Average relative energies (kcal.mol⁻¹) of the ground (S_0) and the excited states ($\pi\pi^*$) of 7Al(H₂O)₄.

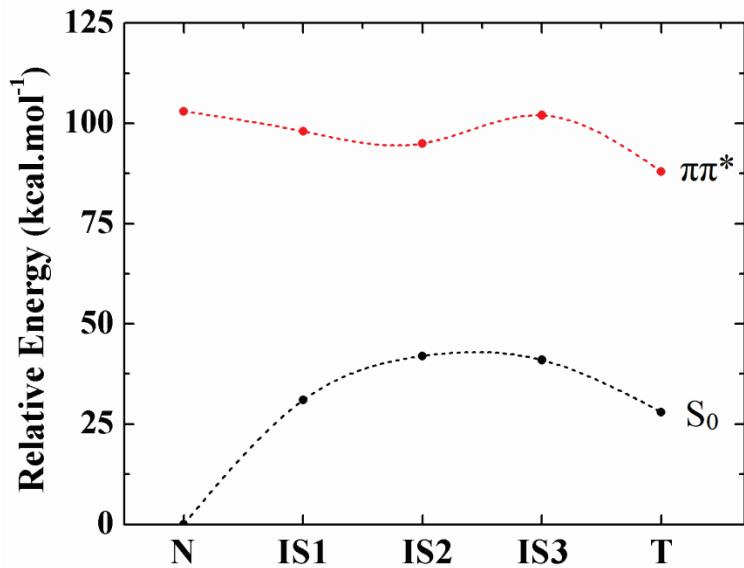


Figure S21. Average relative energies (kcal.mol⁻¹) of the ground (S_0) and the excited states ($\pi\pi^*$) of 7Al(H₂O)₅.

Cartesian Coordinates

Cartesian coordinates of ground-state optimized structures of 7-Al(H₂O)₁₋₅ clusters (in Å). If not stated otherwise, the geometries were optimized at RI-ADC(2)/SVP-SV(P) level.

7Al (H₂O)₁

C	0.0428034	-0.1760973	-0.0117560
C	0.7924739	1.0401631	0.0110259
C	0.0489567	2.2358718	0.0230202
C	-1.3411398	2.1294010	0.0090119
C	-1.9640894	0.8608028	-0.0166625
C	2.2025670	-0.7204051	-0.0090889
C	2.1721176	0.6666081	0.0132715
H	0.5411660	3.2161655	0.0407813
H	-1.9679506	3.0279582	0.0160305
H	-3.0593392	0.7847298	-0.0300107
H	3.0630017	-1.3933197	-0.0167409
H	3.0420101	1.3257910	0.0273268
N	0.9270539	-1.2198477	-0.0236895
H	0.6028757	-2.1913623	-0.0395874
N	-1.2913326	-0.2947980	-0.0267627
H	-1.3794895	-3.4177883	0.8664119
O	-1.1064275	-3.1487429	-0.0181899
H	-1.4985808	-2.2552324	-0.0986940

7Al (H₂O)₁₊₁

C	0.1634863	0.5684837	0.1061004
C	0.3385664	1.9382075	-0.1707783
C	-0.8156126	2.7067894	-0.2953115
C	-2.0364432	2.0705971	-0.1396276
C	-2.0691213	0.6992358	0.1336741
C	2.3450501	0.9552644	-0.0290831
C	1.7630825	2.1571656	-0.2518253
H	-0.7659960	3.7674325	-0.5078366
H	-2.9648964	2.6181388	-0.2270647
H	-3.0215848	0.1972938	0.2547597
H	3.3922467	0.6983698	-0.0070884
H	2.2718936	3.0867212	-0.4502222
N	1.3915707	-0.0073028	0.1889099
H	1.5378460	-0.9808726	0.3696048
N	-0.9937116	-0.0499436	0.2579069
H	-0.0057635	-2.9530376	1.6743002
O	0.1355471	-2.6933431	0.7754049
H	-0.4991985	-1.9975109	0.6027110
H	0.3925822	-5.2919344	-1.3642352
O	-0.2625068	-5.2549776	-0.6852269
H	-0.1447074	-4.4051186	-0.2772629

7Al (H₂O)₂

C	-1.6426241	-0.5919912	0.0223796
C	-0.3051997	-0.1412270	-0.0106723
C	-0.8890039	2.0206372	-0.0862079
C	-2.2504447	1.7063276	-0.0594705
C	-2.6398084	0.3777372	-0.0025660
C	-1.5842232	-2.0316639	0.0758920
C	-0.2685283	-2.3537356	0.0706601
H	-0.5794732	3.0584792	-0.1307040
H	-2.9822563	2.5023082	-0.0825677
H	-3.6881970	0.1071352	0.0205843
H	-2.4134452	-2.7197000	0.1135151
H	0.1947323	-3.3272569	0.1015292
N	0.5086795	-1.2264879	0.0194614
N	0.0756537	1.1241788	-0.0609126
H	2.0046389	1.6520270	0.0197542
O	2.9463662	1.7661584	0.1567919
H	3.0311438	2.1875089	0.9987621
H	1.5164866	-1.2069121	-0.0178003
H	3.4839320	-0.0391778	0.0141664
O	3.4530105	-0.9840437	-0.1329687
H	3.8909390	-1.1251530	-0.9587193

7Al (H₂O)₃ bridged-planar [SVP-SV(P)]

C	-2.1454194	-0.4673089	0.0580084
C	-0.7435124	-0.1824760	-0.0225424
C	-1.0618579	2.0579888	-0.1876277
C	-2.4634750	1.9015574	-0.1269552
C	-3.0234886	0.6315126	0.0021871
C	-2.2644610	-1.8844379	0.1784673
C	-0.9696612	-2.3828088	0.1621683
H	-0.6162099	3.0574232	-0.2839362
H	-3.1011120	2.7910249	-0.1777172
H	-4.1108780	0.4960557	0.0565919
H	-3.1797887	-2.4725852	0.2660822
H	-0.6248996	-3.4175061	0.2281989
N	-0.0620756	-1.3631216	0.0458318
N	-0.1991772	1.0362920	-0.1360863
H	0.9655350	-1.4840455	-0.0469516
H	1.4861496	1.6360621	0.0246039
O	2.3351710	2.1024415	0.2265121
H	2.1859631	2.4214298	1.1238391
H	3.6495829	0.9821611	0.0751688
O	4.2878886	0.2325370	0.0376946
H	4.7988535	0.3219227	0.8489475
H	2.8375391	-2.0730220	-1.2074936
O	2.6416900	-1.8739762	-0.2847815

H	3.2815648	-1.1504037	-0.0857122
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7Al(H₂O)₃ bridged-planar [TZVPP]

C	-2.1377284	-0.4572075	0.0709233
C	-0.7477985	-0.1545063	-0.0389551
C	-1.1032467	2.0681577	-0.2151714
C	-2.4923585	1.8908591	-0.1231527
C	-3.0289702	0.6217405	0.0270046
C	-2.2388978	-1.8684540	0.2000895
C	-0.9476499	-2.3527770	0.1602505
H	-0.6869756	3.0614225	-0.3293289
H	-3.1333628	2.7596791	-0.1675567
H	-4.0980466	0.4725989	0.1045383
H	-3.1331381	-2.4574918	0.3080762
H	-0.5954903	-3.3688606	0.2224994
N	-0.0527069	-1.3263599	0.0218729
N	-0.2173852	1.0658158	-0.1721817
H	0.9596591	-1.4470283	-0.0989656
H	1.4639965	1.6647419	0.0479713
O	2.3352320	2.0901998	0.2336771
H	2.1870034	2.5927992	1.0367645
H	3.6420754	0.9325686	0.2042770
O	4.2751999	0.1867270	0.1390442
H	4.8164911	0.2407668	0.9276582
H	2.8873960	-2.1721241	-1.2662231
O	2.6556079	-1.9181978	-0.3710705
H	3.2950142	-1.2083528	-0.1475435

7Al(H₂O)₃ cyclic nonplanar

C	0.6459314	-0.1663730	0.1384576
C	2.0097010	-0.5165500	-0.1285192
C	2.9237773	0.5434424	-0.2745578
C	2.4335137	1.8424377	-0.1492871
C	1.0655356	2.0648063	0.1169666
C	0.7636033	-2.3810604	0.0557126
C	2.0591805	-1.9417150	-0.1762687
H	3.9853022	0.3573425	-0.4798303
H	3.1014735	2.7043420	-0.2543657
H	0.6826433	3.0895514	0.2151757
H	0.3767473	-3.4018281	0.1014114
H	2.9306056	-2.5735834	-0.3570841
N	-0.0794164	-1.3179141	0.2447045
H	-1.1062031	-1.3693401	0.4213610
N	0.1686945	1.0815231	0.2631115
O	-2.5124847	1.4841829	0.8082879
H	-1.5336279	1.3981163	0.6624663
O	-2.8125229	-1.3156079	0.6478936
H	-3.1287138	-1.0189131	-0.2282973
O	-3.3164736	0.3084696	-1.5613662
H	-2.5131754	0.3691789	-2.0910253

H	-2.9094276	-0.4865494	1.1438193
H	-2.6223234	2.3030688	1.3030188
H	-3.1559259	0.9550377	-0.8486914

7AI (H₂O)₃ bicyclic nonplanar

C	0.5359156	-0.2054069	0.0278741
C	1.9446309	-0.4356872	-0.0075909
C	2.7676783	0.6886862	-0.0357416
C	2.1639625	1.9411153	-0.0278428
C	0.7712402	2.0471863	0.0074858
C	0.8672229	-2.4036973	0.0265366
C	2.1215176	-1.8548045	-0.0071259
H	3.8470563	0.5943881	-0.0643821
H	2.7607742	2.8434323	-0.0513574
H	0.2979038	3.0228724	0.0134670
H	0.5720638	-3.4405068	0.0344600
H	3.0525487	-2.3972451	-0.0299656
N	-0.0929217	-1.4157384	0.0507336
H	-1.1182640	-1.5442110	0.0568487
N	-0.0570493	0.9936389	0.0364419
O	-2.5237964	0.9662810	1.6329339
H	-1.6779787	1.0777706	1.1529159
O	-2.9117240	-1.3657472	0.0354134
H	-3.0088727	-0.7991989	-0.7522887
O	-2.4791508	0.7914474	-1.7795671
H	-1.7012051	1.0167274	-1.2375381
H	-3.0429896	-0.7371350	0.7676358
H	-2.3257251	1.1127848	2.5633367
H	-3.0721339	1.5465591	-1.7036572

7AI (H₂O)₄

C	1.2455132	-0.1757680	0.1151070
C	2.5702289	-0.4753887	-0.2753429
C	3.4253495	0.5978486	-0.4977585
C	2.9209594	1.8776748	-0.3221685
C	1.5905203	2.0403429	0.0678652
C	1.4312989	-2.3764612	0.0067054
C	2.6575988	-1.9128943	-0.3358291
H	4.4541162	0.4439769	-0.7990677
H	3.5409004	2.7492613	-0.4821999
H	1.1910192	3.0386231	0.2062141
H	1.0841227	-3.3948702	0.0808804
H	3.5184285	-2.5061708	-0.5990681
N	0.5765950	-1.3419872	0.2798420
H	-0.3959558	-1.4324779	0.5456825
N	0.7576183	1.0422418	0.2873341
O	-1.9437512	1.5503972	1.1637844
H	-1.0422884	1.3967910	0.8597161

O	-3.9338566	1.5643905	-0.8992994
H	-3.5466649	2.0072798	-1.6391674
H	-1.8733542	2.0430239	1.9677250
H	-3.3137539	1.6697041	-0.1808976
H	-5.1761777	-1.4426046	-0.6736097
O	-4.2788154	-1.2627111	-0.9092005
H	-4.2306184	-0.3165900	-1.0343927
H	-2.8781782	-1.5540596	0.4117976
O	-2.2114319	-1.4093846	1.0799290
H	-2.3278806	-0.5032874	1.3398410

7Al(H₂O)₅

C	1.6868811	-0.1564488	0.1154322
C	2.9762120	-0.4056783	-0.4061605
C	3.7458908	0.6992662	-0.7519583
C	3.1971640	1.9585374	-0.5619162
C	1.9093304	2.0708846	-0.0345411
C	1.9715215	-2.3477595	0.0523182
C	3.1299024	-1.8386581	-0.4329375
H	4.7432605	0.5848706	-1.1582001
H	3.7502540	2.8528024	-0.8148693
H	1.4746130	3.0523450	0.1162714
H	1.6859928	-3.3784336	0.1915354
H	3.9870817	-2.3992970	-0.7694807
N	1.0994602	-1.3463832	0.3860380
H	0.1613614	-1.4713033	0.7469528
N	1.1581549	1.0418783	0.3038951
O	-1.4149999	1.4717845	1.5224536
H	-0.5720663	1.3399678	1.0727247
O	-3.6636320	2.2902564	-0.0550523
H	-2.8955125	2.0669111	0.4671380
H	-1.1952029	1.7418210	2.4018985
H	-4.2066753	2.8301435	0.4983821
H	-4.4688181	-2.6830546	-0.0965285
O	-3.6955748	-2.2324931	-0.3996272
H	-4.0155907	-1.4656634	-0.8739169
H	-2.2855987	-1.8312721	0.8176160
O	-1.6045049	-1.5076773	1.4050099
H	-1.8040837	-0.5901259	1.5457818
H	-4.3846578	0.8853616	-1.0665657
O	-4.6631534	0.1400170	-1.5978247
H	-4.4304673	0.3633023	-2.4862906