Electronic Supplementary Information for

Hydrogen bond network structures of protonated dimethylamine clusters $H^+(DMA)_n$ (n = 3 - 7)

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Contents

Table S1 Relative Gibbs free energies of the stable isomers shown in the main text

Table S2 Calculated H-bonded NH stretching vibrational frequencies and H-bonding structure parameters of the stable isomers shown in the main text

Table S3 Band frequencies in the experimental spectra of bare $H^+(DMA)_n$ (n = 3 - 7)

Table S4 Band frequencies in the experimental spectra of $H^+(DMA)_n$-Ar (n = 3 - 7)

Figure S1 All calculated stable isomer structures of $H^+(DMA)_3$

Figure S2 All calculated stable isomer structures of $H^+(DMA)_4$

Figure S3 All calculated stable isomer structures of $H^+(DMA)_5$

Figure S4 All calculated stable isomer structures of $H^+(DMA)_6$

Figure S5 All calculated stable isomer structures of $H^+(DMA)_7$

Figure S6 Calculated IR spectra of the most stable **L** isomers at each temperature of $H^+(DMA)_3$

Figure S7 Calculated IR spectra of the most stable **L** and **C** isomers at each temperature of $H^+(DMA)_4$

Figure S8 Calculated IR spectra of the most stable **L**, **C**, and **Ct** isomers at each temperature of $H^+(DMA)_5$

Figure S9 Calculated IR spectra of the most stable **L**, **C**, and **Ct** isomers at each temperature of $H^+(DMA)_6$

Figure S10 Calculated IR spectra of the most stable **L**, **C**, and **Ct** isomers at each temperature of $H^+(DMA)_7$

Figure S11 Correlation plot between calculated H-bonded NH stretching vibrational frequencies and H-bonding structure parameters of the stable isomers of $H^+(DMA)_n$ (n = 3 – 7)

Table S1. Relative Gibbs free energies of stable isomers of $H^+(DMA)_n$ (n = 4 - 7) shown in the main text. Temperature is set to 0, 100, and 200 K. The level of theory is B3LYP+D3/6-311+G(d, p). All energies are in kJ/mol and zero-point energy corrected. The energies at 0 K are identical with the relative electronic energies. **L**, **C**, and **Ct** mean the structure types, linear, cyclic, and cyclic with a "tail", respectively (see Fig. 1 in the main text). **Ct**-A is a **Ct** structure with a six-membered ring moiety, and **Ct**-B is with a five-membered ring moiety. Relative energy of n = 3 is not shown here, since only **L** structures were found (see Fig. S1).

	relative free energy (kJ/mol)		
	0 K	100 K	200 K
	***n* = 4**		
L	0	0	0
C	5.9	5.7	5.8
	***n* = 5**		
L	0.3	0	0
C	0	2.6	6.5
Ct	6.9	8.7	12.0
	***n* = 6**		
L	5.9	1.8	0
C	0	0	4.7
Ct	2.5	2.8	7.9
	***n* = 7**		
L	7.7	1.9	0
C	1.2	1.2	8.0
Ct-A	0	0	6.3
Ct-B	4.4	5.4	11.8

Table S2. Calculated H-bonded NH stretching vibrational frequencies and H-bonding structure parameters of the stable isomers of $H^+(DMA)_n$. The calculated H-bonded NH stretching frequencies, H-bond lengths (N···H distances), N-H bond lengths, and H-bond coordination status of the H-bonded (H-accepting) site of the most stable structures shown in Figs. 3-5, 7, and 8 in the main text are presented. Correlation between these NH frequency and these structure parameters is shown in Fig. S11.

	Frequency (cm^{-1})	H-bond length (Å)	N-H bond length (Å)	Bonded site
		***n* = 3**		
L	2508	1.745	1.071	A sym.
	2430	1.740	1.071	A asym.
		***n* = 4**		
L	3031	1.961	1.034	A
	2591	1.772	1.063	A
	2021	1.623	1.102	AD
C	3255	2.310	1.021	AA sym.
	3212	2.198	1.023	AA asym.
	2525	1.741	1.071	AD sym.
	2366	1.712	1.077	AD asym.
		***n* = 5**		
L	3059	1.978	1.033	A sym.
	3056	1.977	1.033	A asym.
	2291	1.668	1.087	AD sym.
	2159	1.667	1.087	AD asym.
C	3306	2.381	1.017	AA
	3181	2.104	1.025	AA
	3092	2.007	1.031	AD
	2434	1.719	1.074	AD sym.
	2170	1.655	1.091	AD asym.
Ct	3241	2.218	1.022	AAD
	3153	2.086	1.027	AAD
	3123	2.027	1.028	A
	2505	1.737	1.071	AD sym.
	2288	1.687	1.083	AD aysm.
		***n* = 6**		
L	3126	2.009	1.028	A
	3066	1.980	1.032	A
	2960	1.912	1.039	AD
	2305	1.678	1.083	AD sym.
	2108	1.643	1.093	AD asym.
C	3280	2.274	1.019	AA sym.
	3254	2.202	1.020	AA asym.
	3086	2.016	1.031	AD
	3039	1.963	1.034	AD
	2379	1.707	1.078	AD sym.
	2172	1.657	1.090	AD aysm.
Ct	3298	2.344	1.018	AAD
	3136	2.036	1.028	A asym.
	3109	2.044	1.029	AAD sym.

	3095	2.011	1.030	AD
	2358	1.689	1.081	AD sym.
	2216	1.672	1.085	AD asym.
		***n* = 7**		
L	3130	2.012	1.028	A
	3124	2.014	1.028	A
	2977	1.923	1.037	AD sym.
	2973	1.920	1.038	AD asym.
	2265	1.661	1.088	AD sym.
	2125	1.653	1.090	AD asym.
C	3329	2.500	1.016	AA
	3213	2.102	1.022	AA
	3199	2.155	1.024	AD
	3063	1.973	1.032	AD
	3008	1.941	1.035	AD
	2330	1.683	1.083	AD sym.
	2181	1.660	1.087	AD asym.
Ct-A	3274	2.254	1.020	AAD sym.
	3210	2.140	1.023	AAD asym.
	3161	2.079	1.026	A
	3077	2.011	1.031	AD
	3006	1.941	1.036	AD
	2382	1.707	1.078	AD sym.
	2130	1.645	1.093	AD asym.
Ct-B	3314	2.409	1.017	AAD
	3212	2.111	1.023	A
	3162	2.074	1.026	AD
	3122	2.079	1.029	AAD
	3079	2.004	1.031	AD
	2365	1.685	1.082	AD sym.
	2241	1.682	1.082	AD asym.

Table S3. Band frequencies in the experimental spectra of bare $H^+(DMA)_n$ (n = 3 - 7). All units are in cm^{-1}. The positions of shoulder bands are shown in parentheses.

n = 3	n = 4	n = 5	n = 6	n = 7	assignment
3331	3339	-	-	-	free NH str.
-	3118	3160	3181	3227	NH str. H-bonded to
-	-	-	3134	3136	A or AD site
(3013)	2979	(3005)	2970	2967	
(2988)	2950	2974	2944	2940	
2958	2927	2943	(2921)	2871	
(2917)	2889	2884	2876	2843	CH str.
(2890)	2810	2848	2845	2794	
2821	-	2802	2798	-	
2709	-	-	-	-	

Table S4. Band frequencies in the experimental spectra of bare $H^+(DMA)_n$-Ar (n = 3 - 7). All units are in cm^{-1}. The positions of shoulder bands are shown in parentheses.

n = 3	n = 4	n = 5	n = 6	n = 7	assignment
3331	3339	3342	-	-	free NH str.
-	-	3295	3305	3321	NH str. H-bonded to
-	-	3241	3276	3296	AA or AAD site
-	-	-	-	3286	
-	3112	3143	3143	3229	NH str. H-bonded to
-	-	-	-	3134	A or AD site
3010	2981	3002	3004	3003	
2987	2951	2976	2974	(2971)	
2958	(2903)	2947	2945	2941	
2893	2884	2925	2870	2868	CH str.
2813	2845	2900	2841	2839	
2706	2812	2882	2797	2794	
-	2802	2846	-	-	
-	-	2801	-	-	
3120	-	-	-	-	Combination/overtone?

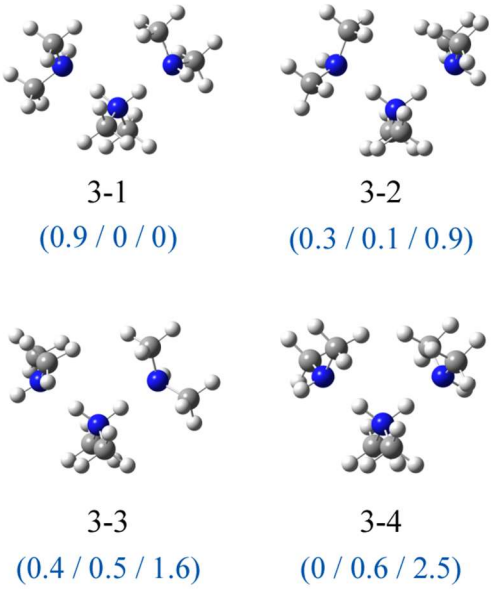


Figure S1 All the calculated stable isomer structures of $H^+(DMA)_3$. Only the **L** type structures were found. The relative free energies at 0/100/200 K are shown in parentheses (all units are in kJ/mol). The level of theory is B3LYP+D3/6-311+G(d, p).

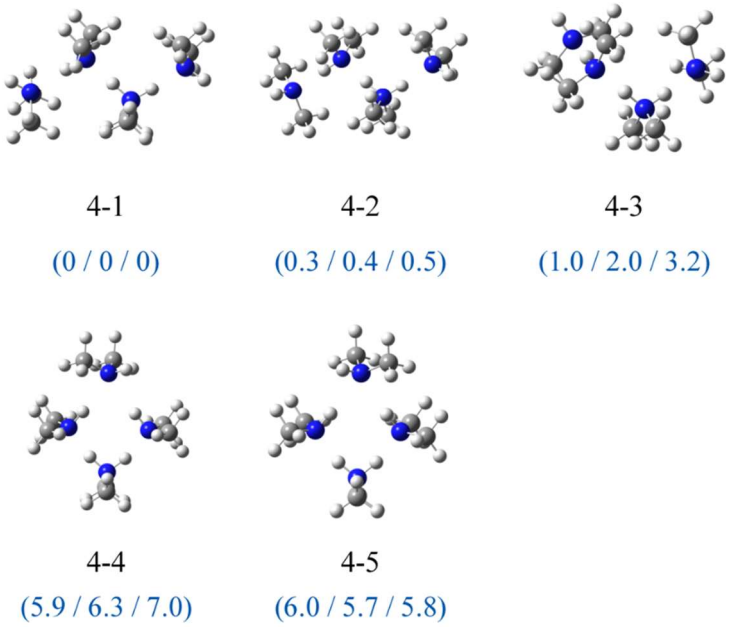


Figure S2 All the calculated stable isomer structures of $H^+(DMA)_4$. The **L** and **C** type structures were found. The relative energies at 0/100/200 K are shown in parentheses (all units are in kJ/mol). The level of theory is B3LYP+D3/6-311+G(d, p).

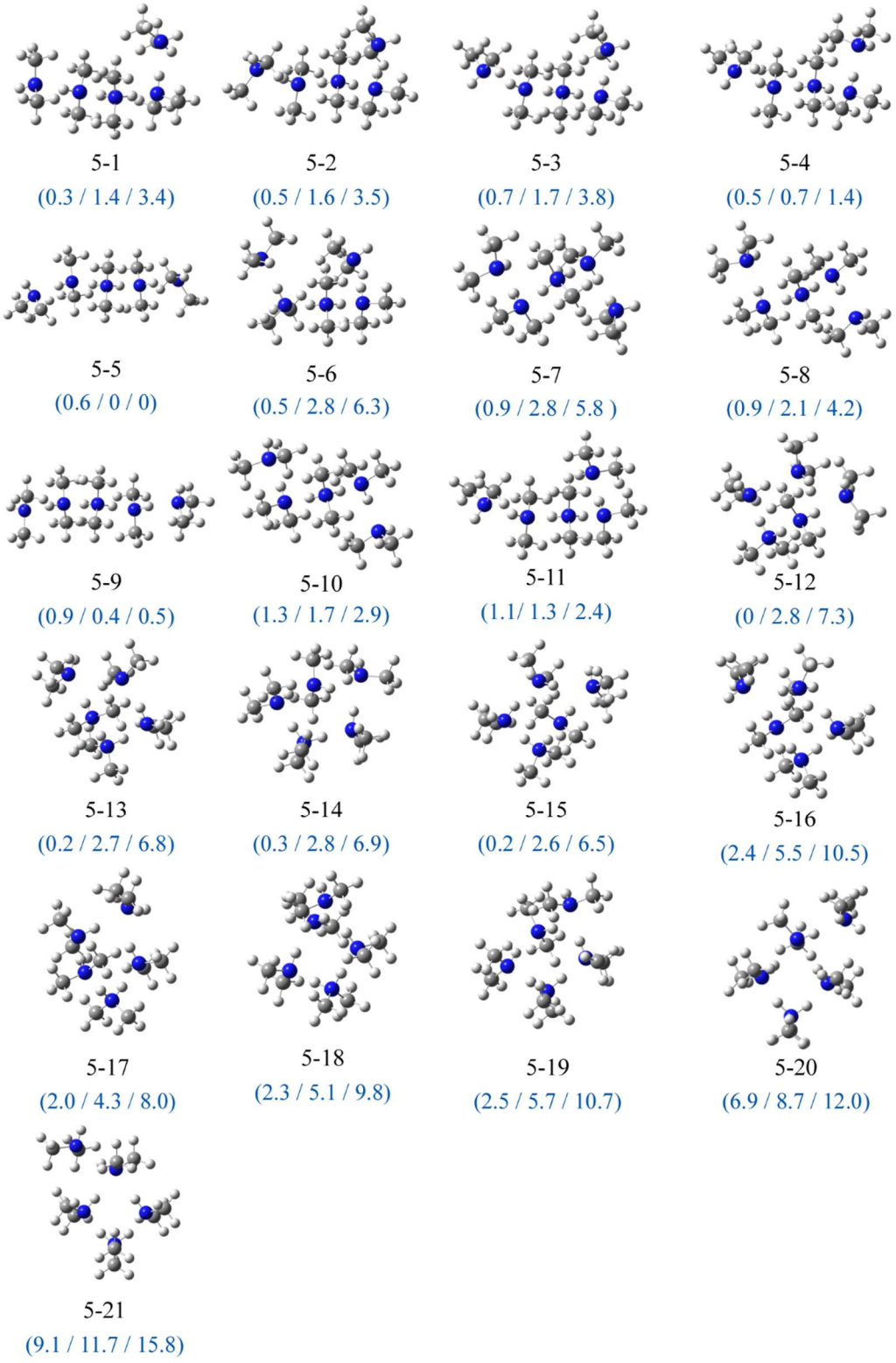
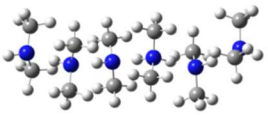


Figure S3 All the calculated stable isomer structures of $H^+(DMA)_5$. The **L**, **C**, and **Ct** type structures were found. The relative free energies at 0/100/200 K are shown in parentheses (all units are in kJ/mol). The level of theory is B3LYP+D3/6-311+G(d, p).

6-1
(5.9 / 4.7 / 7.4)



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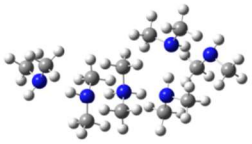
(6.5 / 2.0 / 0.4)



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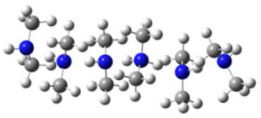
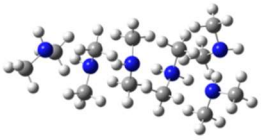
(6.6 / 2.9 / 2.3)



6-4
(6.7 / 1.8 / 0)

6-5
(7.1 / 4.0 / 4.2)

6-6
(7.4 / 3.1 / 1.9)



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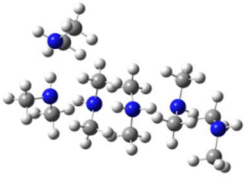
(7.7 / 4.3 / 4.4)



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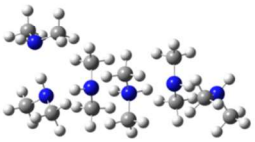
(8.0 / 2.9 / 0.6)



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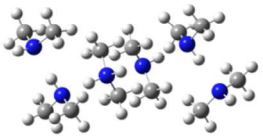
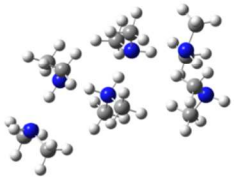
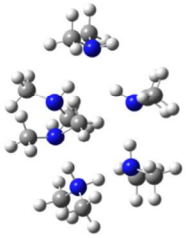
(8.0 / 3.2 / 1.3)



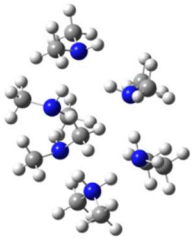
6-10
(8.3 / 4.3 / 3.3)



6-11
(11.0 / 8.3 / 9.4)



6-12
(0 / 0 / 4.7)



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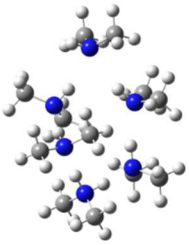
(0.2 / 0.8 / 6.2)



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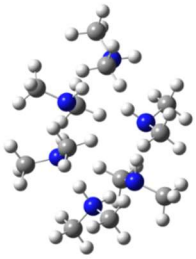
(1.5 / 2.3 / 8.3)



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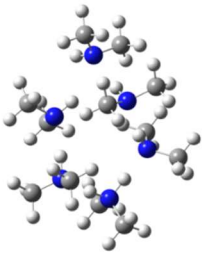
(2.0 / 1.3 / 5.0)



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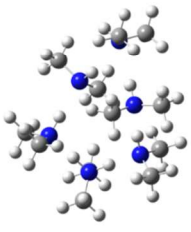

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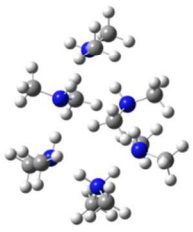
(2.4 / 1.7 / 5.6)



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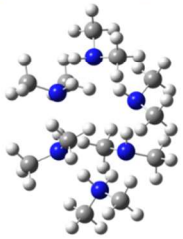
(3.0 / 2.9 / 7.4)



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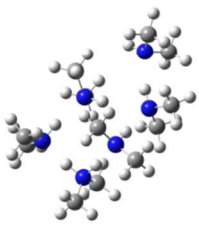
(4.2 / 4.2 / 9.1)



6-20
(2.5 / 2.8 / 7.9)

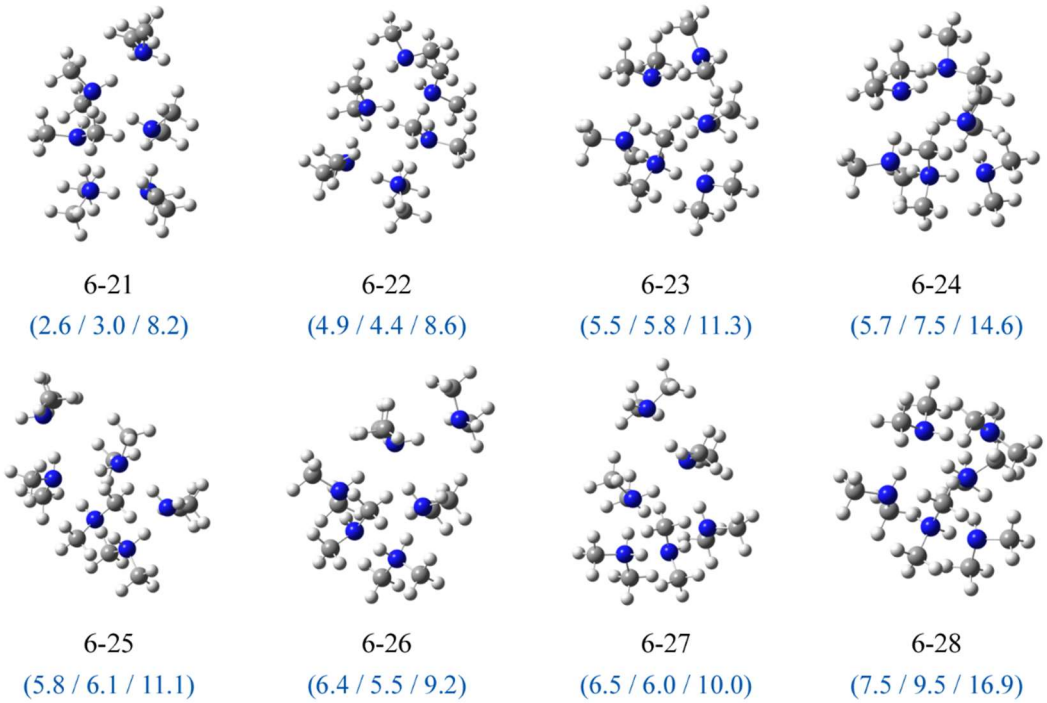
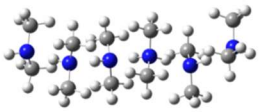


Figure S4 All the calculated stable isomer structures of $H^+(DMA)_6$. The **L**, **C**, and **Ct** type structures were found. The relative free energies at 0/100/200 K are shown in parentheses (all units are in kJ/mol). The level of theory is B3LYP+D3/6-311+G(d, p).

7-1

(7.7 / 6.7 / 12.0)



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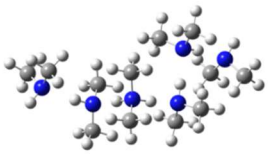
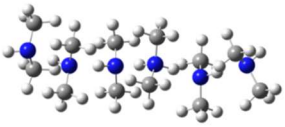
(8.0 / 1.9 / 0.4)



7-3

(8.3 / 7.2 / 12.4)



7-4

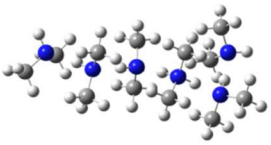
(8.6 / 2.8 / 1.8)

7-5

(8.7 / 4.3 / 4.9)

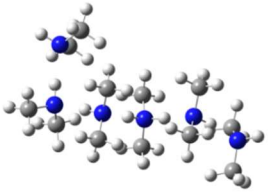
7-6

(9.3 / 2.4 / 0)



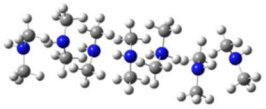
7-7

(9.3 / 4.6 / 4.9)



7-8

(11.0 / 5.6 / 5.0)



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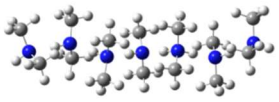
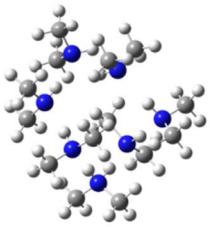
(11.1 / 4.4 / 2.3)



7-10

(11.5 / 4.1 / 1.1)



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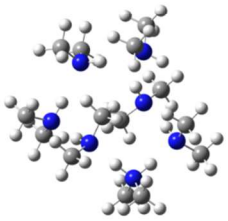
(1.4 / 1.2 / 8.0)



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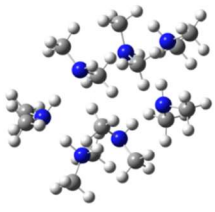
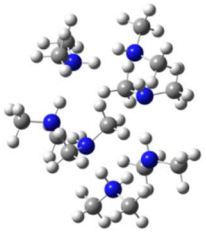
(1.2 / 1.6 / 9.0)



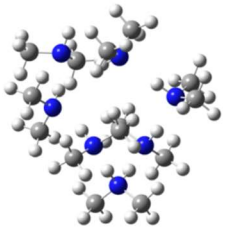
7-13

(1.9 / 2.4 / 10.0)



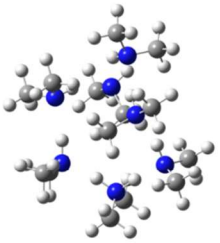
7-14

(2.9 / 2.8 / 9.6)



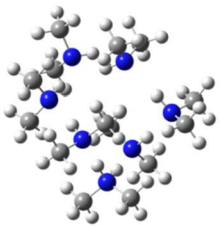
7-15

(3.1 / 3.0 / 9.7)

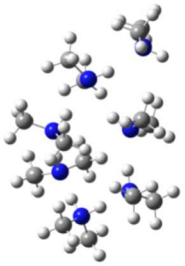


7-16

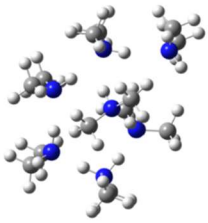
(7.5 / 9.0 / 18.2)



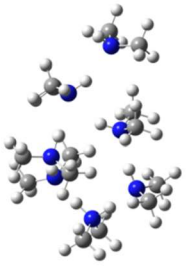
7-17
(1.6 / 1.5 / 8.4)



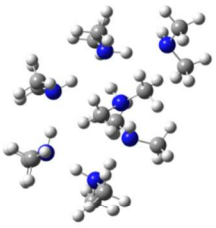
7-18
(0 / 0 / 6.9)



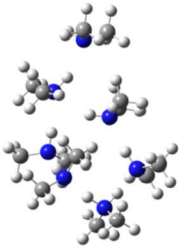
7-19
(1.0 / 2.4 / 11.3)



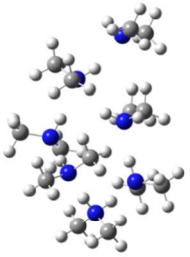
7-20
(1.7 / 0.7 / 6.3)



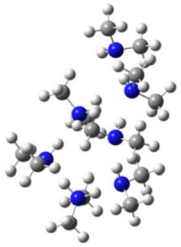
7-21
(1.8 / 1.9 / 9.2)



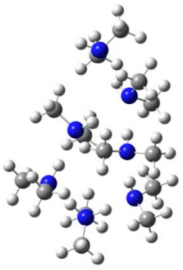
7-22
(2.0 / 1.4 / 7.5)



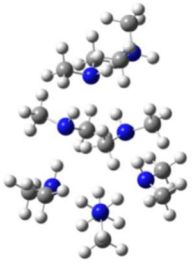
7-23
(2.1 / 1.6 / 7.9)



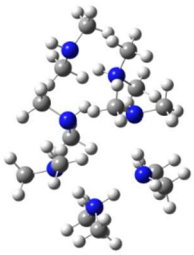
7-24
(2.9 / 1.6 / 7.0)



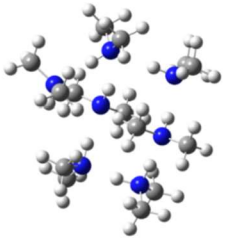
7-25
(4.2 / 3.1 / 8.7)



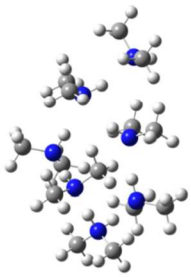
7-26
(4.4 / 2.9 / 8.3)



7-27
(4.3 / 3.2 / 8.9)

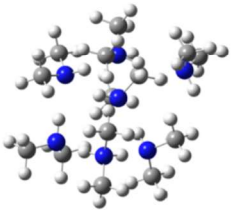


7-28
(5.6 / 7.2 / 16.6)

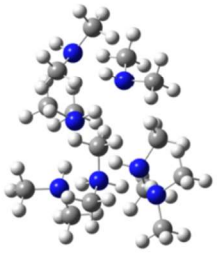


7-29
(0.8 / 0.3 / 6.7)

7-30
(4.4 / 5.4 / 13.9)



7-31
(5.4 / 6.9 / 16.1)



7-32
(5.8 / 6.5 / 14.5)

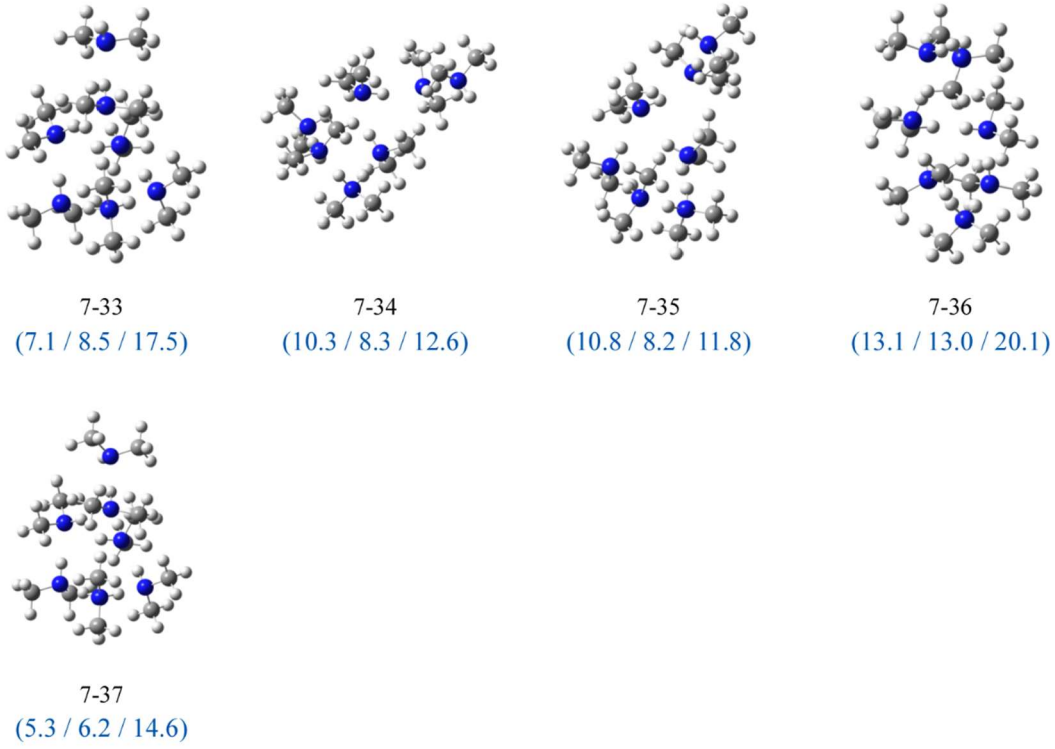


Figure S5 All the calculated stable isomer structures of $H^+(DMA)_7$. The **L**, **C**, and **Ct** type structures were found. The relative free energies at 0/100/200 K are shown in parentheses (all units are in kJ/mol). The level of theory is B3LYP+D3/6-311+G(d, p).

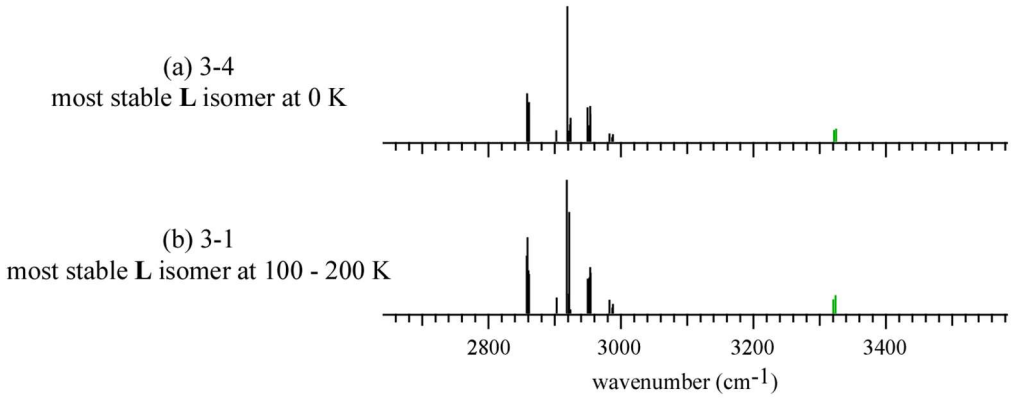


Figure S6 Calculated IR spectra of the most stable **L** isomers of $H^+(DMA)_3$ at (a) 0 and (b) 100 - 200 K. The isomer structures are displayed in Fig. S1. Isomer 3-1 is that shown in Fig. 3 in the main text. The green- and black-colored bars are the free NH stretching and CH stretching vibrational bands, respectively.

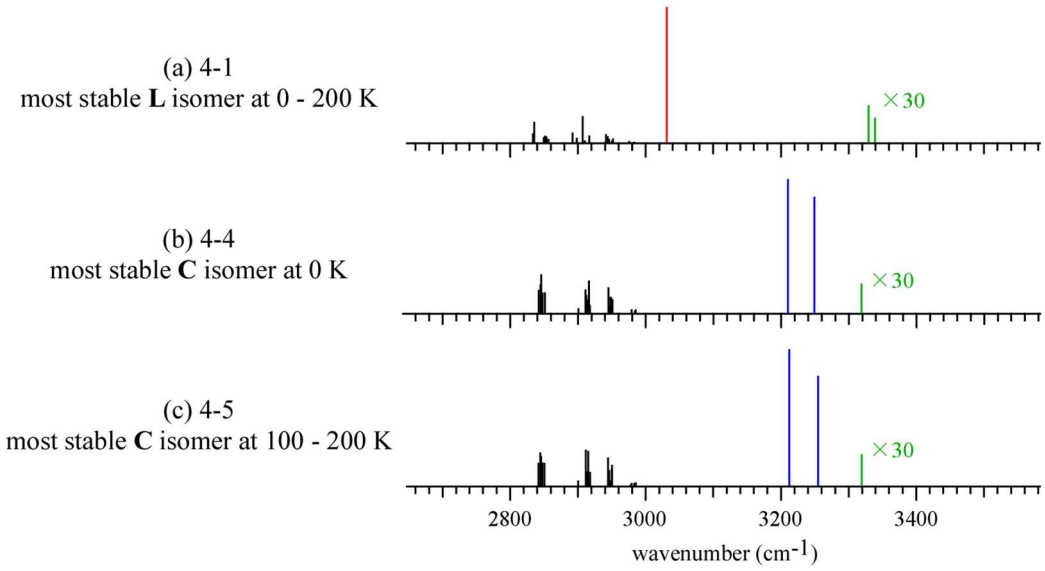


Figure S7 Calculated IR spectra of the most stable **L** and **C** isomers of $H^+(DMA)_4$ at 0, 100, and 200 K. The isomer structures are displayed in Fig. S2. Isomers 4-1 and 4-5 are those shown in Fig. 4 in the main text. The green-, blue-, red-, and black-colored bars are the free NH stretching, NH stretching H-bonded to AA site, NH stretching H-bonded to A site, and CH stretching vibrational bands, respectively.

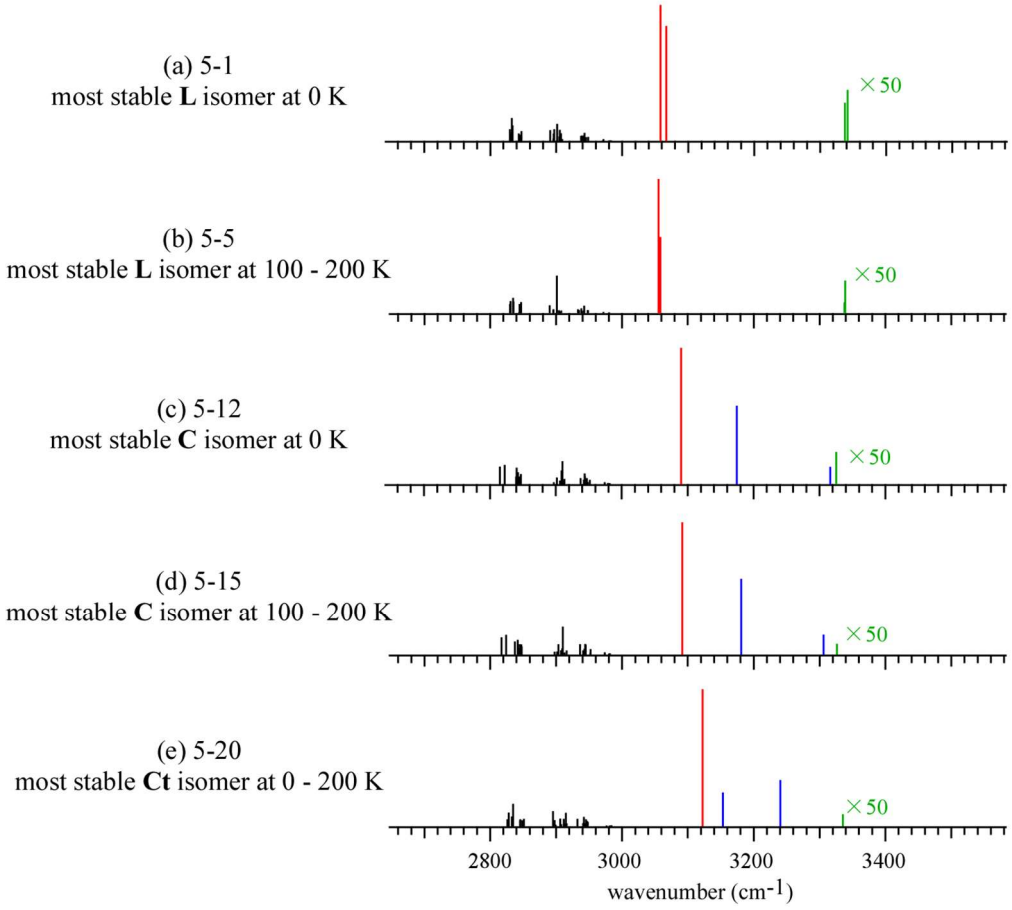


Figure S8 Calculated IR spectra of the most stable **L**, **C**, and **Ct** isomers of $H^+(DMA)_5$ at 0, 100, and 200 K. The isomer structures are displayed in Fig. S3. Isomers 5-5, 5-15, and 5-20 are those shown in Fig. 5 in the main text. The green-, blue-, red-, and black-colored bars are the free NH stretching, H-bonded NH stretching to AA sites, H-bonded NH stretching to A or AD sites, and CH stretching vibrational bands, respectively.

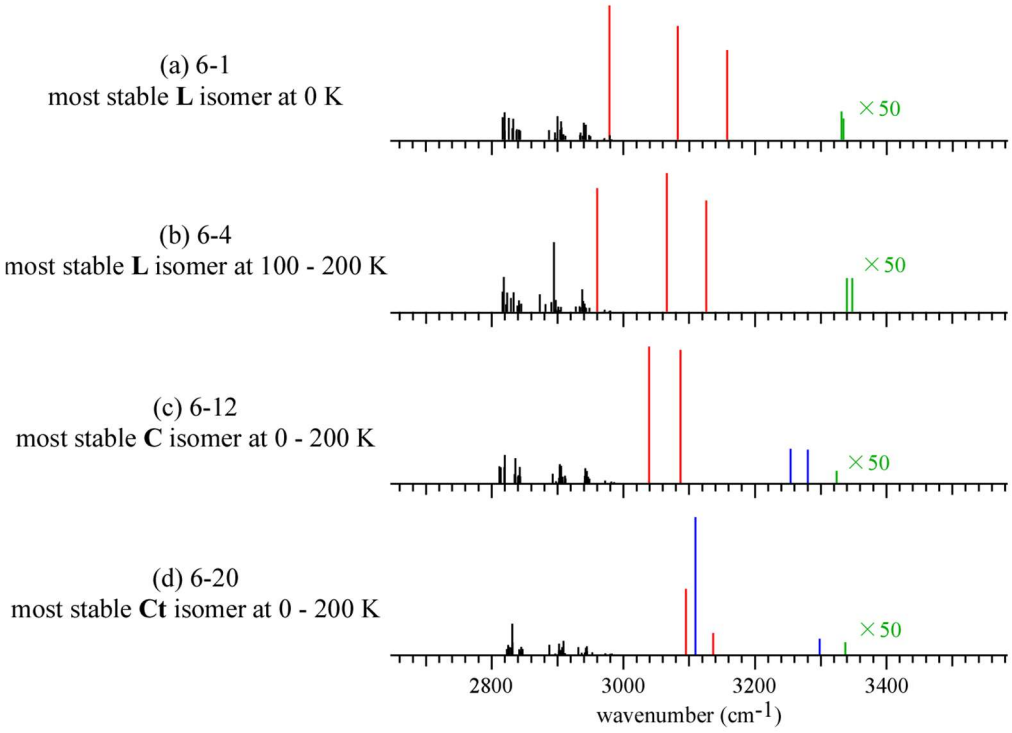


Figure S9 Calculated IR spectra of the most stable **L**, **C**, and **Ct** isomers of $H^+(DMA)_6$ at 0, 100, and 200 K. The isomer structures are displayed in Fig. S4. Isomers 6-4, 6-12, and 6-20 are those shown in Fig. 7 in the main text. The green-, blue-, red-, and black-colored bars are the free NH stretching, NH stretching H-bonded to AA sites, NH stretching H-bonded to A or AD sites, and CH stretching vibrational bands, respectively.

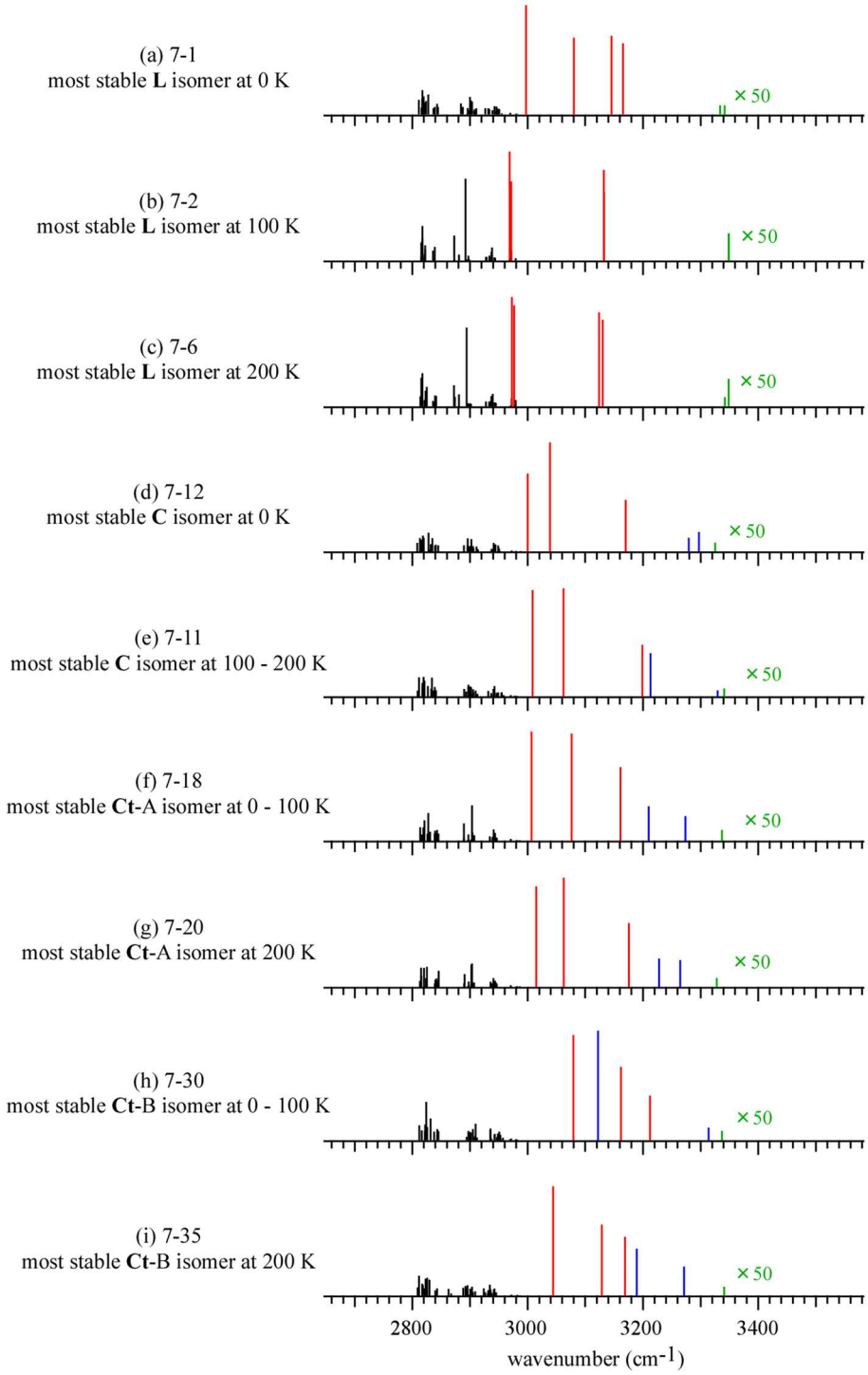


Figure S10 Calculated IR spectra of the most stable **L**, **C**, **Ct**-A and **Ct**-B isomers of $H^+(DMA)_7$ at 0, 100, and 200 K. The isomer structures are displayed in Fig. S5. Isomers 7-6, 7-11, 7-18, and 7-30 are those shown in Fig. 8 in the main text. The green-, blue-, red-, and black-colored bars are the free NH stretching, NH stretching H-bonded to AA or AAD sites, NH stretching H-bonded to A or AD sites, and CH stretching vibrational bands, respectively.

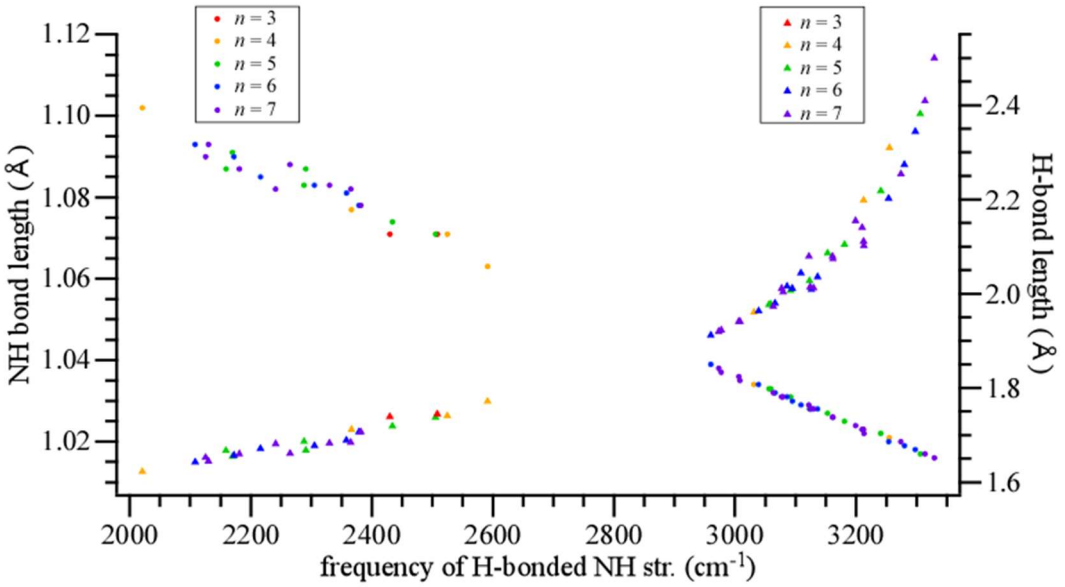


Figure S11. Correlation plot of the calculated H-bonding parameters of the stable structures of $H^+(DMA)_n$ (n = 3 – 7) with the H-bonded NH stretching vibrational frequencies. This plot is based on the data listed in Table S2. Correlation of the H-bonded NH stretching vibrational frequency with the N-H bond length is represented by circle (●), while that with the H-bond length (N···H distance) is represented by triangle (▲). It is clear that the H-bonded NH stretching vibrational frequency is correlated to both the N-H bond length and H-bond length.