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Effect of self association on N-H stretching force constants of ammonia

M C Shivaglal, P Mohandas and Surjit Singh*
Department of Chemistry, Indian Institute of Technology, Madras, India

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Abstract : Molecular orbital calculations have been carried out on various clusters of ammonia exhibiting long chain and cyclic association. The variation in the N-H stretching force constants for the hydrogen bonded and free N-H bonds of ammonia molecules forming such clusters are discussed. The reduction in the hydrogen bonded N-H stretching force constants are interpreted in terms of stabilisation energies per hydrogen bond and cooperativity effect.

Keywords : MO calculations, ammonia, force constants, self association.

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1. Introduction

Self association studies of ammonia have been reported [1-13] using microwave, infrared and Raman spectroscopy as well as infrared dissociation, CARS and molecular beam electric deflection methods. Crystal structure of ammonia was studied by X-ray [14] and neutron diffraction [15] methods and it was shown that in the solid phase ammonia molecules are closely packed in cubic structure such that each molecule is hydrogen bonded to its six nearest neighbours, three through its hydrogen atoms and three through its lone pair of electrons. The N-H...N angle was found to be 164°. It is reported [3] that on passing from the gaseous to liquid phase, the υ_1 and υ_3 stretching frequencies of ammonia in the IR spectra are lowered by 40 and 30 cm^{-1} respectively whereas υ_2 frequency is raised by 62 cm^{-1}. Matrix isolation IR and Raman spectroscopic studies of ammonia have also been reported [4-7].

Various experimental and theoretical studies have led to contradictory conclusions regarding the stability of open verses cyclic structure of dimers and trimers of ammonia. Pimental *et al* [4] assigned the high frequency band for ammonia in solid nitrogen matrix to the monomer, and the low frequency bands to the linear dimer and its higher aggregates. Suzer and Andrews [5] proposed the presence of an antisymmetric cyclic dimer and open chain trimer. Barnes [6] studied IR and Raman spectra of ammonia trapped in argon and nitrogen matrices

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* Author for correspondence

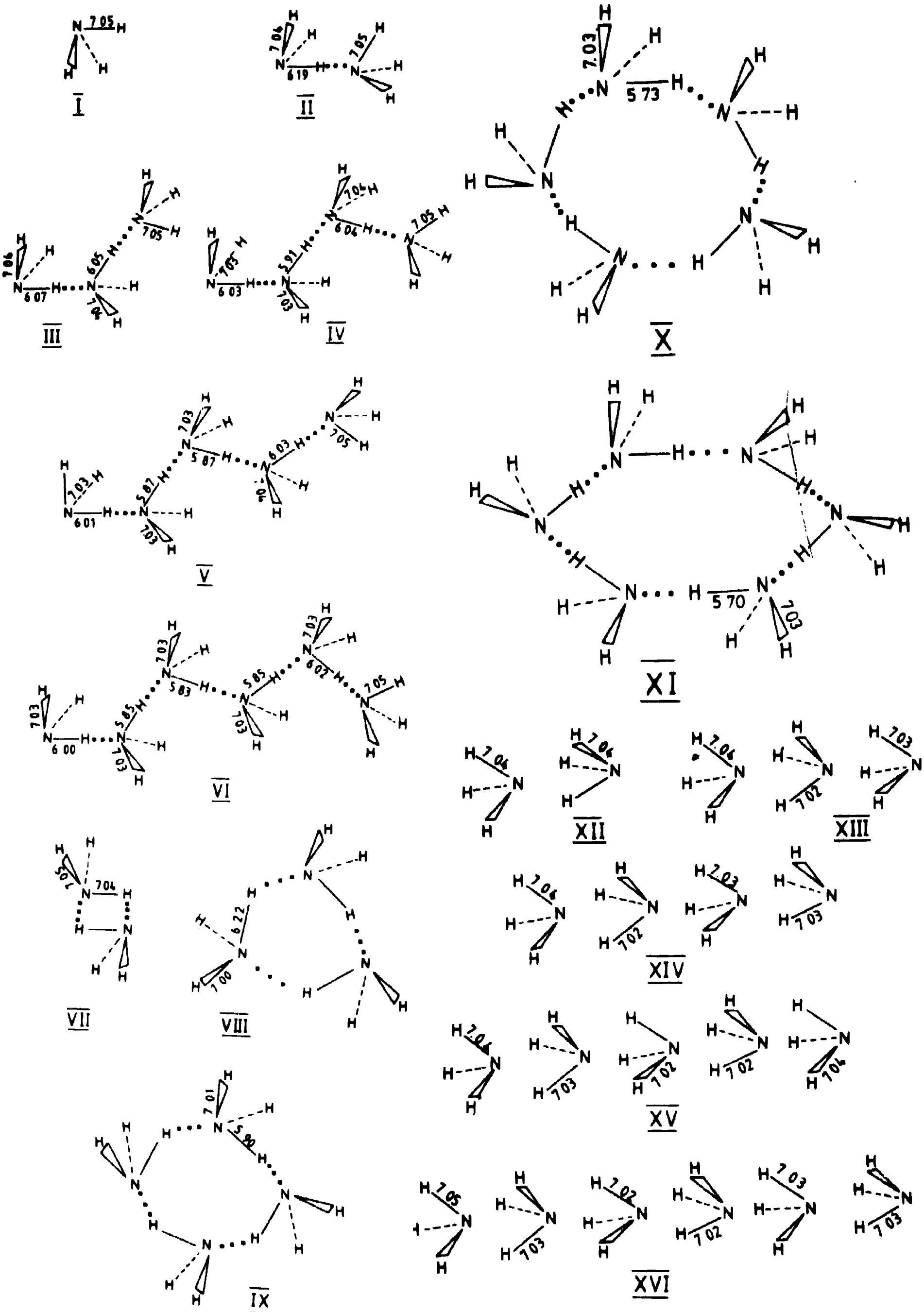

Figure 1. Structures of various clusters of ammonia showing open, cyclic and trifurcated self association. The open configurations actually deviate from linear N-H...N hydrogen bonds which are schematically shown as linear for convenience. The values given along the bonds show scaled N-H stretching force constants in mdyne Å^{-1}.

and the relative intensities of the bands showed the existence of an open dimer and a cyclic trimer. Based on vibrational analysis, Perchard *et al* [7] proposed the existence of a weak non classical bent hydrogen bond in the dimer. Snels *et al* [9] carried out IR dissociation study of ammonia clusters $(NH_3)_n$ (n = 3 to 6) and predicted cyclic structures for ammonia polymers. Odutola and Dyke [13] carried out molecular beam electric deflection studies of ammonia polymers and predicted a linear structure for the dimer and cyclic structures for the polymers. On the basis of *ab initio* calculation on dimer and trimers of ammonia, Jean [16] reported that the cyclic trimer shows evidence of cooperativity effect on hydrogen bonding due to polarisation of the central molecule by its nearest neighbours. According to the author trimer destabilisation energy due to non linearity of the three hydrogen bonds is lower than the gain in energy arising from the polarisation of the three molecules in the cyclic trimer. It was proposed that higher polymers are also expected to be cyclic as the non linearity decreases along with the increase in the order of polymerisation in these clusters. Latajka and Scheiner [17] and Sadlej and Lapanski [18] carried out *ab initio* calculation on ammonia dimer and proposed a cyclic structure based on potential energy surface calculations. Frisch *et al* [19] carried out *ab initio* calculations on the ammonia dimer and found that linear dimer was more stable than the cyclic structure. The vibrational frequencies obtained for the monomer and dimer are in agreement with the trends in the decrease in the frequency by formation of hydrogen bond in the dimer.

As an extension to our work on stretching force constants of molecular clusters [20-23] we have calculated N-H stretching force constants for $(NH_3)_n$ where n = 1 to 6. Various structures involving linear, cyclic and trifurcated hydrogen bonds have been considered. Since *ab initio* molecular orbital calculations are difficult to perform on such large molecular clusters, we have carried out semiempirical molecular orbital calculation, the details of the method of calculations are discussed elsewhere [24].

2. Results and discussion

Various structures of clusters of ammonia considered are shown in Figure 1. The numbers given along the bonds denote the N-H stretching force constants in mdyne $Å^{-1}$. The semi empirical MO calculations are found to overestimate the stretching force constants; the calculated N-H stretching force constant values are therefore scaled down by a factor of

Table 1. The stabilisation energy ΔE and stabilisation energy per hydrogen bond ΔE/HB for the cyclic and linear polymers of ammonia

Species	ΔE, kcal mol^{-1}		ΔE/HB kcal mol^{-1}	
	cyclic	linear	cyclic	linear
Dimer	0.577	5.77	0.29	5.77
Trimer	15.05	12.29	5.02	6.15
Tetramer	27.03	19.13	6.75	6.38
Pentamer	35.38	26.03	7.05	6.51
Hexamer	42.28	32.99	7.08	6.60

2.058 which was derived by comparing calculated value for monomer NH_3 molecule in the present studies with the experimental value reported in the literature [25].

The stabilisation energies of the dimers (structures II, VII and XII in Figure1) given in Table 1 show that the non linear open dimer is more stable than the cyclic dimers. The open dimer is found to be non linear as shown by X-ray and neutron diffraction studies [14, 15]. The hydrogen bonded N-H stretching force constant of the open dimer (structure II) is reduced to 6.19 mdyne Å^{-1} from its monomer (structure I) value of 7.05 mdyne Å^{-1}. The non hydrogen bonded N-H stretching force constants of the individual ammonia molecules do not show any significant reduction. The hydrogen bonded as well as the free N-H stretching force constants of the cyclic and trifurcated ammonia dimers do not show appreciable changes in their values when compared to the monomer value. Perchard *et al* [7] calculated the force constants and frequencies of ammonia dimer with a non linear open structure using *ab initio* calculations. The hydrogen bonded N-H stretching force constant was found to be 6.20 mdyne Å^{-1} and free N-H stretching force constant 6.25 mdyne Å^{-1} compared to the monomer value of 6.36 mdyne Å^{-1}, which follows trends similar to the values of force constants obtained in the present studies.

It is also observed that the open trimer of ammonia is more stable than the cyclic trimer; the hydrogen bond energies (Table 1) are found to be 6.15 and 5.02 kcal mol^{-1} respectively. The N-H stretching force constant values for the hydrogen bonded N-H bond of the central molecule (structure III) is found to be 6.05 mdyne Å^{-1} in the case of open trimer whereas it is found to be 6.22 mdyne Å^{-1} for the cyclic trimer. Perchard *et al* [7] suggested open structure for dimer and trimer of ammonia: It is found that, whereas open dimer and trimer structures are more stable than the cyclic structures the reverse is true for tetramer and higher polymers. For cyclic hexamer the stabilisation energy per hydrogen bond is found to be 7.05 kcal mol^{-1} compared to 6.60 kcal mol^{-1} for the open hexamer. These observations can be well augmented by the observed trends in the optimised geometrical parameters of the various ammonia polymers $(NH_3)_n$ given in Table 2. In the cyclic hexamer the hydrogen bonded N-H bond distance is found to be 1.091Å compared to 1.068Å in the case of monomer as well as the non hydrogen bonded N-H bond of the polymers. Further, in the case of cyclic dimer the N-H...N angle is found to be 119.53° which increases to a value of 180.0° for the cyclic hexamer thus showing a relaxed hydrogen bonded structures for the

Table 2. The optimized values of geometrical parameters for cyclic polymares of ammonia $(NH_3)_n$.

Species	R_{N-H}, Å	<N-H...N, deg.	$R_{N...H}$, Å
Dimer	1.068	119.53	1.732
Trimer	1.081	152.36	1.715
Tetramer	1.087	167 48	1.627
Pentamer	1.090	173.99	1 576
Hexamer	1.091	180.00	1.562

larger molecular clusters. The N...H distance is found to be 1.715Å for the cyclic dimer and 1.562Å for the cyclic hexamer. These observations show that when one passes from a cyclic dimer to hexamer, the strain in the hydrogen bond is released thus allowing a better and closer approach of the molecules in the cluster to form stronger hydrogen bond.

In order to appreciate the effect of cooperativity on hydrogen bonded N-H stretching force constants similar to the definitions given in our earlier publications [20-23], we represent the open polymers of ammonia as A_m...N-H...D_n where A_m and D_n denotes the number of electron acceptor and electron donor molecules preceding and succeeding the N-H bond under consideration. The hydrogen bonded N-H stretching force constants of the ammonia polymers (A_m...N-H...D_n) are given in Table 3. With increasing values of *m* and *n*, the hydrogen bonded N-H stretching force constants show a systematic reduction in their values. The hexamer (structure VI) A_2...N-H...D_3 is found to have the lowest value of the force constant among the open polymers which is found to be 5.83 mdyne $Å^{-1}$. The hydrogen bonded and free N-H stretching force constants of the cyclic polymers of ammonia $(NH_3)_n$ are shown in Table 4. The force constants show decrease in their values while going from monomer to hexamer. The cyclic hexamer (structure XI) is found to have the lowest value of 5.70 mdyne $Å^{-1}$. The hydrogen bonded N-H stretching force constant for cyclic hexamer (5.70 mdyne $Å^{-1}$) is lower than that of the open hexamer (5.83 mdyne $Å^{-1}$). We have earlier defined [20, 21] the cooperativity effect (CE) using the relationship CE = $(\Delta F/F) \times 100$, where F represents the hydrogen bonded N-H stretching force constant for the dimer and ΔF represents the difference between the hydrogen bonded N-H force constant of the dimer (F) and the hydrogen bonded N-H stretching force constant of the N-H bond in the polymer under consideration. The CE values for ammonia clusters are given in Table 5. The CE is found to increase with increase in the values of *m* and *n* in the ammonia polymers (A_m...N-H...D_n) and with increasing values of *n* in cyclic polymers, $(NH_3)_n$. It is found to

Table 3. The N-H stretching force constants, mdyne $Å^{-1}$ of open polymers of ammonia (A_m...N-H...D_n).

m\n	0	1	2	3	4	5
0	7.05	6.185	6.069	6.025	6.006	6.001
1	7.05	6.054	5.908	5.865	5.845	
2	7.045	6.040	5.870	5.826		
3	7.045	6.025	5.850			
4	7.045	6.020				
5	7.045					

Table 4. The N-H stretching force constants for cyclic polymers of ammonia $(N\text{-}H_3)_n$.

n =	2	3	4	5	6
Bonded N-H	7.036	6.220	5.899	5.729	5.695
Free N-H	7.045	7.002	7.007	7.026	7.026

be 7.93 and 5.81 respectively for the cyclic $(NH_3)_6$ and open hexamer (A_2...N-H...D_3), thus showing a greater cooperativity effect on the N-H stretching force constant of the cyclic ammonia hexamer. The negative values of cooperativity effects for cylic dimer and trimer of ammonia also indicates lesser stability of cyclic structures than open chain structures in these cases. The free N-H force constants are not affected to an appreciable extent which is similar to the observations made in the case of clusters of water [20], methanol [21], acetonitrile [22] and formamide [23].

Table 5. (a) The CE values for A_m ..N-H. D_n polymers of ammonia.

m\n	1	2	3	4
1	2.12	4.48	5.18	5.50
2	2.36	5.11	5.81	
3	2.59	5.42		
4	2.67			

(b) The CE values for the cyclic polymers of ammonia $(NH_3)_n$.

CE	-13.73	-0.55	4.63	7.38	7.93

The crystal structure of ammonia shows [14, 15] that in solid state it has cubic close packed structure in which each ammonia molecule is surrounded by six nearest neighbours-three through its own N-H bonds and three through its lone pair of electrons. In Figure 2

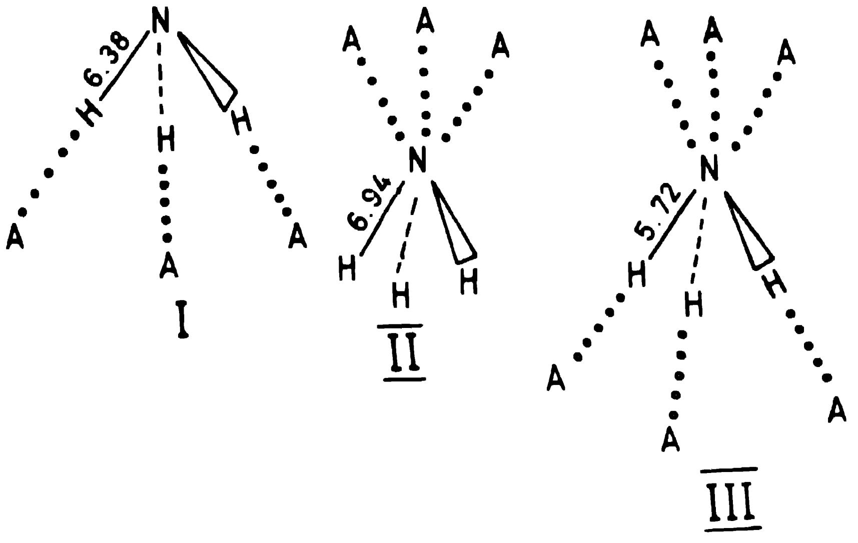

Figure 2. Structures of clusters of ammonia with multiple hydrogen bonds similar to those found in solid phase. The values given along the bonds show scaled N-H stretching force constants in mdyne $Å^{-1}$.

are shown three structures of ammonia clusters leading to this configuration. It can be noticed that when the ammonia molecule is hydrogen bonded through its lone pair of electrons (structure II) the N-H stretching force constant reduces to 6.93 mdyne $Å^{-1}$ whereas it is reduced to 6.38 mdyne $Å^{-1}$ when the hydrogen bonding takes place through the N-H bonds of the NH_3 molecule. The force constant reduces further to 5.72 mdyne $Å^{-1}$ when the interaction takes place through its lone pair of electrons as well as its three N-H bonds (structure III). The significant reduction in stretching force constant for structure III can be explained on the basis of cooperativity effect by which the polarisation of the central molecule takes place by the six nearest neighbours through the lone pair of electrons and the three N-H bonds. The cooperativity effect (CE) in this case is found to be 7.53.

3. Conclusions

The stabilisation energy as well as the force constant calculations support that ammonia dimer and trimer have open non linear (bent) hydrogen bonded structures. The trend in the decrease of the hydrogen bonded N-H stretching force constant as well as the stabilisation energy per hydrogen bond shows that up to trimer, ammonia clusters prefer open structures where as from tetramer to hexamer they prefer cyclic structures. The geometrical parameters like the N-H distance, N...H distance and the N-H...N angle shows why ammonia prefers a cyclic structure from tetramer to hexamer. The calculated N-H stretching force constant and the CE value of the six coordinated ammonia molecule explain the existence of such structures in the solid state.

Acknowledgments

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