

## THEORETICAL STUDIES OF INVERSION IN AMMONIA MOLECULE\*

BY E. RADZIO

Quantum Chemistry Laboratory, Institute of Basic Problems of Chemistry, University of Warsaw\*\*

(Received August 6, 1976)

The inversion of an ammonia molecule associated by a hydrogen bond with a second one is investigated. Linear and bifurcated structures of the dimer are considered. Inversion of the proton donor ammonia in a linear dimer is shown to be more advantageous. The potential energy curves as well as the hydrogen bond energies for both structures are also shown. The results predict that a linear dimer is more stable than the bifurcated one.

### 1. Introduction

It is well known that in an ammonia molecule the inversion is observed. The height of the inversion barrier can be estimated from spectroscopic data. So far several authors have analysed the vibrational spectrum of the  $\nu_2$  mode of ammonia and proposed different values for the inversion barrier [1-4]. The work of Swalen and Ibers [3] provides the commonly accepted value of the barrier height.

Theoretical calculations of the inversion barrier have been performed by numerous authors [5-11]. In most of the papers the problem of the correlation energy contribution to the inversion barrier has been discussed. The calculations presented by Rauk et al. as well as by Stevens clearly show the ability of the Hartree-Fock model to yield a reliable value for the inversion barrier if a large basis set of Gaussian or Slater functions is used.

It seems, however, impossible to predict quantitatively the inversion splitting of the vibrational levels using the Hartree-Fock potential. The values of this splitting are too large because the potential curve obtained from the Hartree-Fock calculations is too narrow as compared with the experimentally derived one [6].

---

\* This work was partly supported by the Polish Academy of Sciences within the project MR.I.9.

\*\* Address: Pracownia Chemii Kwantowej, Instytut Podstawowych Problemów Chemii, Uniwersytet Warszawski, Pasteura 1, 02-093 Warszawa, Poland.

The present work is mainly devoted to an investigation of the influence of the hydrogen bond on the inversion and on the height of the inversion barrier in the ammonia molecule. The linear and bifurcated structures of the ammonia dimer are examined (Fig. 1). All calculations have been carried out by means of the SCF method.

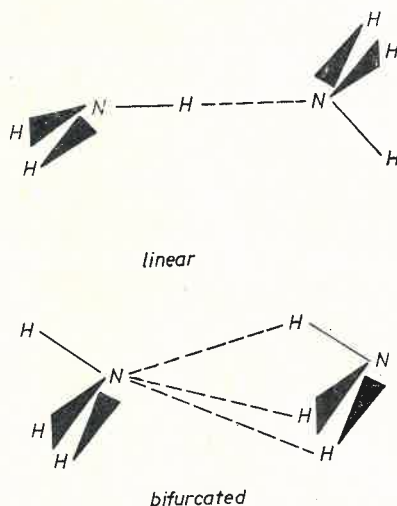


Fig. 1. Structures of ammonia dimers

## 2. Monomer calculations

The results for monomer ammonia are listed in Table I<sup>1</sup>. In the present calculations the lobe Gaussian basis set (6s, 3p for nitrogen, 3s for hydrogen) has been employed [12]. For pyramidal ammonia, the experimental geometry has been assumed. In one calcula-

TABLE I

Results for the ammonia molecule

Symmetry	$E_{\text{total}}$	Barrier	Dipole moment <sup>1</sup>	Reference
$C_{3v}$ <sup>2</sup>	-55.8160		1.88	present work
$D_{3h}$ <sup>3</sup>	-55.7994	10.4		
$D_{3h}$ <sup>4</sup>	-55.7984	11.1		
$C_{3v}$	-56.2219			[6]
$D_{3h}$	-56.2117	5.9	—	exp. [5]
$C_{3v}$	-56.578	5.8	1.48	

<sup>1</sup> Dipole moments are expressed in debyes. <sup>2</sup>  $R_{\text{NH}} = 1.9117$  a.u.,  $\angle \text{HNH} = 106.7^\circ$  [5]  
<sup>3</sup>  $R_{\text{NH}} = 1.8807$  a.u.,  $\angle \text{HNH} = 120^\circ$ . <sup>4</sup>  $R_{\text{NH}} = 1.9117$  a.u.,  $\angle \text{HNH} = 120^\circ$ .

<sup>1</sup> In all Tables the values of the N-N distances (denoted by  $R$ ), total monomer energies are expressed are expressed in a.u. and those of barrier heights as well as of interaction energies in kcal/mole.

tion, the N-H distance in the planar molecule has been considered to be different from that accepted for the pyramidal one. The difference between the values of the N-H distances in both conformations has been assumed to be equal to that calculated by Stevens who had provided the best theoretical value of the barrier [6]. In the second calculation, the N-H distances in both conformations have been considered to be equal.

For comparison the experimental and the best SCF results for ammonia are also reported in Table I.

It is seen that the calculated barrier is too high as compared with the experimental value and with the best SCF result. Attempts to improve it by extending the set (the d orbitals on nitrogen and the s orbitals fixed in the middle of the N-H bond have been added) failed. Also, some larger basis sets proposed by other authors [13, 14] appeared to yield quite bad results. It is believed, however, that the basis set employed in the present work can correctly describe the relative effect of the hydrogen bond formation on inversion in the ammonia molecule.

The geometry assumed for the planar molecule appears to be of some consequence in calculating of the barrier height. As seen from Table I, if one uses different N-H distances for both conformations the barrier height obtained is slightly better.

### 3. Hydrogen bond properties

Two structures of the ammonia dimer have been considered (Figure 1). The interaction energies as well as the equilibrium N-N distances (denoted by  $R_e$ ) for both structures are listed in Table II. Fig. 2 shows the shapes of the potential energy curves as functions of the N-N distance (denoted by  $R$ ).

It is seen that the linear structure is predicted to be more stable than the bifurcated one. This result agrees with experiment because the linear dimer is observed to exist in

TABLE II

Hydrogen bond properties

$R_e$ <sup>1</sup>	Interaction energy	Reference
	$(\text{NH}_3)_2$ linear	
5.75	-11.6	present work
6.6 (3.49) <sup>2</sup>	-2.7	[15]
6.37 (3.37)	-3.5	[16]
6.2 (3.28)	-4.3	[19]
5.82 (3.08)	—	[17]
—	-4.4	exp. [18, 21]
	$(\text{NH}_3)_2$ bifurcated	
5.7	-5.15	present work

<sup>1</sup>  $R_e$  denotes the equilibrium N-N distance. <sup>2</sup> The values in parentheses are expressed in Å.

gaseous ammonia. It also confirms the semiempirical considerations of other authors [20]. Until now, however, no ab initio calculations have been carried out for the bifurcated structure.

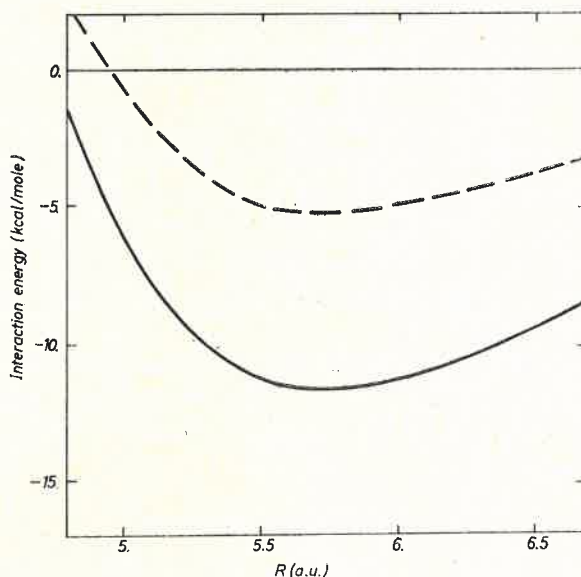


Fig. 2. Potential energy curves for ammonia dimers: — potential energy curve for the linear dimer, ----- potential energy curve for the bifurcated dimer

The interaction energies for the linear structure are overestimated as compared with experimental and other SCF results. The value of  $R_e$  (5.75 a. u.) is smaller than the results obtained by Kollman and Allen (6.6 a. u.) [15], Kollman et al. (6.2 a. u.) [19] and Baird (6.37 a. u.) [16] but very close to that calculated by Thorsley (5.82 a. u.) [17].

#### 4. Inversion in an ammonia dimer

In the linear ammonia dimer, two inversion motions can be considered, i. e., the inversion of the proton donor or of the proton acceptor. The results for both cases are listed in Table III.

It is seen that for  $R < R_e$  the barrier slightly decreases in both cases as compared with the value for the isolated molecule. On the other hand, at an intermediate  $R$  the barrier for the proton donor almost does not change and for the proton acceptor it decreases significantly.

Inversion in the proton acceptor should be, however, energetically unprofitable because of the presence of the hydrogen bond. After the inversion three hydrogen atoms of the proton acceptor closely approach the proton forming a bond and the dimer becomes unsatble. Fig. 3 illustrates the inversion paths for both cases and for monomer inversion.

TABLE III

Inversion barriers in linear dimer <sup>1</sup>	
	Barrier
Monomer <sup>2</sup>	10.4
Dimer I <sup>2, 3</sup>	9.8
Dimer II <sup>2, 3</sup>	9.8
Dimer I <sup>2, 4</sup>	10.6
Dimer II <sup>2, 4</sup>	8.9
Monomer <sup>5</sup>	11.1
Dimer I <sup>3, 5</sup>	10.1
Dimer II <sup>3, 5</sup>	10.4
Dimer I <sup>4, 5</sup>	11.1
Dimer II <sup>4, 5</sup>	9.4

<sup>1</sup> In all dimer calculations the experimental geometry for the pyramidal molecule is assumed (See footnote 2 to Table I). Dimer I (II) denotes the inversion in the proton donor (proton acceptor). <sup>2</sup> The N-H distance in the planar molecule is considered to be different from the value for the pyramidal one (See footnote 3 to Table I). <sup>3</sup>  $R = 5$  a.u. <sup>4</sup>  $R = 5.75$  a.u. <sup>5</sup> The N-H distance in the planar molecule is equal to the value for the pyramidal molecule (See footnote 4 to Table I).

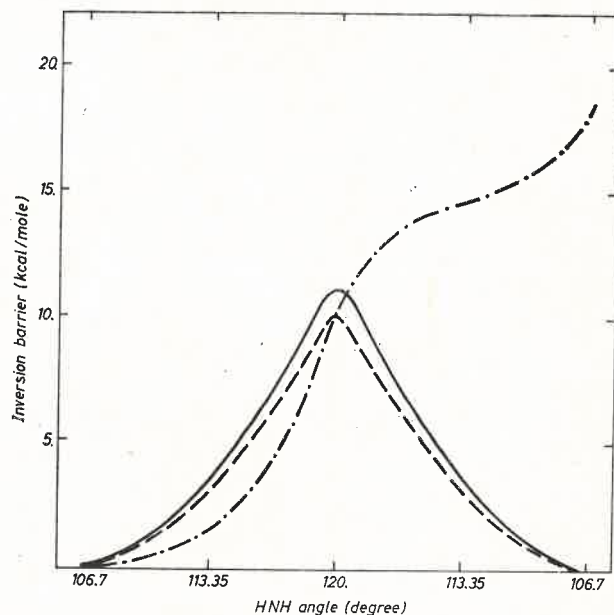


Fig. 3. Inversion paths in the linear dimer.  $R = 5$  a.u. The N-H distances are considered to be constant during the inversion and equal to the value for the pyramidal conformation. — inversion path for the monomer, - - - inversion path for the proton donor, - · - · - inversion path for the proton acceptor

It is seen that the inversion path for the proton donor is symmetric like that for the monomer as expected. The inversion path for the proton acceptor is quite different. It has no maximum corresponding to the barrier but rather an inflection point at the HNH angle equal to  $120^\circ$ . Such a shape of the curve confirms the suggestions mentioned above.

In the bifurcated dimer a double simultaneous inversion in both molecules and a single inversion in the ammonia acting as an electron acceptor have also been studied. In the electron donor inversion cannot be considered. After this inversion the hydrogen atoms of both molecules would be close together. Such a dimer structure would be energetically very unprofitable. All results for the inversion in the bifurcated dimer are summarized in Table IV.

TABLE IV

Inversion barriers in bifurcated dimer	
	Barrier
Monomer <sup>1</sup>	10.4
Dimer I <sup>2</sup>	24.5
Dimer I <sup>3</sup>	31.7
Dimer II <sup>2</sup>	
C <sub>3v</sub>	—
D <sub>3h</sub>	15.1
C <sub>3v</sub>	6.95

<sup>1</sup> In all calculations reported in Table IV the N-H distance is assumed to be different from the value for the pyramidal one (see footnote 3 to Table I). Dimer I (II) denotes the double (single) inversion. <sup>2</sup>  $R = 6.7$  a.u. <sup>3</sup>  $R = 5.7$  a.u.

The barrier height for the inversion in the electron acceptor appears to be higher than that for the isolated molecule. Such inversion is also energetically unprofitable. After inversion, the mutual orientation of both molecules is quite disadvantageous and their interaction becomes repulsive.

The barrier corresponding to double inversion is very high particularly at intermediate intermolecular distances as seen from Table IV. This is due to the high energy of a dimer composed of two planar ammonias.

From the known values of the barrier heights, the relative changes of the inversion frequencies corresponding to the first two vibrational levels can be estimated using the theory given by Dennison and Uhlenbeck [1, 2]. Assuming a simple shape of the potential curve which consists of two equal parabolas connected by a straight line these authors have obtained the following formulas for the inversion splittings

$$\Delta_0/v_0 = (2\alpha/\pi^{\frac{1}{2}}) \exp [-\alpha^2 - 2(x_0 - \alpha)(\alpha^2 - 1)^{\frac{1}{2}}],$$

$$\Delta_1/v_0 = [4(\alpha^3 - \alpha)/\pi^{\frac{1}{2}}] \exp [-\alpha^2 - 2(x_0 - \alpha)(\alpha^2 - 3)^{\frac{1}{2}}],$$

where  $\Delta_0$  — inversion splitting of the ground state,  $\Delta_1$  — inversion splitting of the first excited state,  $v_0$  — vibrational frequency,  $x_0 = (4\pi^2\mu v_0/h)^{\frac{1}{2}}q$ ,  $q$  — height of the ammonia pyramid,  $\mu$  — reduced mass,  $\alpha = \sqrt{\frac{2V}{v_0}}$ ,  $V$  — barrier height.

In the present work the above formulas have been applied to evaluate the inversion frequencies using the barrier heights calculated for the monomer and for the ammonia molecule acting as a proton donor in the linear dimer at  $R < R_e$ . The parameters  $\nu_0$ ,  $\mu$  and  $q$  have been taken from the work of Weiss and Strandberg [2].

For the absolute values of the inversion frequencies, the values which have been obtained are too low in both cases. One can expect, however, that their relative changes are more reliable. It appears that a reduction of 9% in barrier height, as for inversion in the proton donor, (assuming equal N—H distances for both conformations) causes the inversion frequencies splittings to increase by about 10% for the zeroth vibrational level and about 15% for the first excited one.

### 5. Conclusions

Theoretical studies performed in the present work predict that, in the linear dimer, the hydrogen bond slightly affects inversion in the ammonia molecule. The inversion in the ammonia acting as a proton donor appears to be the most advantageous one. Such a result has been expected. At intermolecular distance shorter than those corresponding to the minimum, the barrier height for this case decreases by about 9% (assuming equal N—H distances for both conformations) as compared with the monomer value. This rather small reduction of the barrier height can affect the vibrational spectrum of the  $\nu_2$  mode for ammonia and change the inversion splittings by about 10% and 15% for the zeroth and first vibrational levels, respectively. Such changes should be observable in the spectroscopic measurements.

The inversion in the ammonia acting as a proton acceptor is quite unprofitable though in this case the barrier height is also lowered. The binding proton repels the hydrogens of the proton acceptor and inversion is not allowed.

In the bifurcated dimer the double as well as the single inversions are energetically unprofitable.

The author is very indebted to Professor Włodzimierz Kołos for numerous and very valuable discussions and for reading and commenting on the manuscript. The author also thanks Professor Jan Stankowski for calling her attention to the problem and for interesting remarks on the manuscript. Acknowledgements are also due to Dr Krzysztof Pecul and Mr. Jan Andzelm for help in performing the numerical calculations.

### REFERENCES

- [1] D. Dennison, G. E. Uhlenbeck, *Phys. Rev.* **41**, 313 (1932).
- [2] M. T. Weiss, M. W. P. Strandberg, *Phys. Rev.* **83**, 567 (1951).
- [3] J. D. Swalen, J. A. Ibers, *J. Chem. Phys.* **36**, 1914 (1962) and references therein.
- [4] R. Moccia, L. Randaccio, *J. Chem. Phys.* **45**, 4303 (1966).
- [5] A. Rauk, L. C. Allen, E. Clementi, *J. Chem. Phys.* **52**, 4133 (1970) and references therein.
- [6] R. M. Stevens, *J. Chem. Phys.* **55**, 1725 (1971) and references therein.
- [7] R. E. Kari, I. G. Csizmadia, *J. Chem. Phys.* **56**, 4337 (1972).
- [8] N. C. Dutta, M. Karplus, *Chem. Phys. Lett.* **31**, 455 (1975).

- [9] R. M. Stevens, *J. Chem. Phys.* **61**, 2086 (1974).
- [10] R. Alrichs, F. Driessler, H. Lischka, V. Staemmler, W. Kutzelnigg, *J. Chem. Phys.* **62**, 1235 (1975).
- [11] N. P. Marullo, B. Munsch, *J. Mol. Struct.* **27**, 271 (1965).
- [12] S. Huzinaga, *J. Chem. Phys.* **43**, 1293 (1965).
- [13] C. Ritchie, H. King, *J. Chem. Phys.* **47**, 564 (1967).
- [14] L. Snyder, H. Basch, *Molecular Wavefunctions and Properties Tabulated from SCF Calculations in a Gaussian Basis Set*, J. Wiley and Sons, New York 1972.
- [15] P. Kollman, L. C. Allen, *J. Am. Chem. Soc.* **93**, 4991 (1971).
- [16] N. C. Baird, *Intern. J. Quantum Chem. Quantum Biology Symposia*, **S1**, 49 (1974).
- [17] D. J. Thorsley, *B. Sc. Thesis, University of Western Ontario*, London, Canada 1973, quoted in Ref. [16].
- [18] J. Lambert, *Discus. Faraday Soc.* **15**, 226 (1953).
- [19] P. A. Kollman, J. Mc Kelvey, A. Johanson, S. Rothenberg, *J. Am. Chem. Soc.* **97**, 955 (1975).
- [20] J. Hoyland, L. Kier, *Theor. Chim. Acta* **15**, 1 (1969).
- [21] G. Pimentel, A. L. Mc Clellan, *The Hydrogen Bond*, W. H. Freeman, San Francisco 1960.