An Electron Diffraction Investigation of the Molecular Structure of Ethylenimine

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In the three membered ring compounds such as cyclopropane, ethylene oxide, ethylene sulfide and ethylenimine, the isoelectronic groups $H_2C\langle$, $O\langle$, $S\langle$ and $HN\langle$ bear a resemblance to each other, so that the structural features for these molecules are identical except for these groups.

Since two sp hybrid atomic orbitals may not be at an angle less than 90° to each other, the bonding orbitals which constitute rings CCC, CCO, CCS and CCN can not point directly at each other, but they are bent, forming the "banana bond"[1].

Electron diffraction and microwave spectrum investigations have reported the molecular structures of these ring compounds in which the nuclear distances of C–C were in most cases shorter than the normal C–C single bond distance, 1.54 Å.

By the electron diffraction method, the C–C distances were 1.53 ± 0.03 Å[2], 1.54 Å[3] and 1.515 ± 0.02 Å[4] in cyclopropane, and 1.46 ± 0.03 Å[5] in ethylene oxide. Further, by the microwave spectroscopy the C–C distance was 1.472 Å[6] in ethylene oxide, 1.492 Å[6] in ethylene sulfide and 1.480 Å[7] in ethylenimine respectively. The HCH angles have been found to be about 116°[4] and 117°[6,7], which are larger than the tetrahedral angle, 109.5°.

In this report the results of the electron diffraction study of ethylenimine by the sector-microphotometer method are described and compared with those of the microwave spectrum study[7] (Table I).

TABLE I. MOLECULAR STRUCTURE OF ETHYLENIMINE BY MICROWAVE SPECTROSCOPY[7]

C–C	1.480 Å	$\angle C_2NH$	112°
C–N	1.488 Å	$\angle CCH_2$	159°25′
C–H	1.083 Å	$\angle HCH$	116°41′
H–H	1.000 Å (assumed)		

Experimental

Ethylenimine was kindly furnished by Professor Y. Iwakura, Tokyo Institute of Technology; its boiling point was 55°C.

The electron diffraction instrument in the Department of Chemistry, Faculty of Science, the University of Tokyo[8] was used for the diffraction experiment. It incorporates with r^2-sector which

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[1] C. A. Coulson and W. E. Moffit, *Phil. Mag.*, **40**, 1 (1949).

[2] L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.*, **59**, 1223 (1937).

[3] O. Bastiansen and O. Hassel, *Tids. Kjemi Bergvesen Met.*, **6**, 71 (1946).

[4] H, Pfeiffer, Ph. D. thesis, California Institute of Technology, 1948.

[5] M. Igarashi, This Bulletin, **26**, 330 (1953).

[6] G. L. Cunningahm, A. W. Boyd, R. J. Mayer, W. D. Gwinn and W. I. LeVan, *J. Chem. Phys.*, **19**, 679 (1951).

[7] T. E. Turner, V. C. Fiora, W. M. Kendrick and B. L. Hicks, ibid., **21**, 564 (1953); T. E. Turner, V. C. Fiora and W. M. Kendrick, ibid., **23**, 1966 (1955).

[8] K. Kuchitsu, This Bulletin, **30**, 391 (1956).

is rotated rapidly during exposure. Diffraction photographs were obtained on Fuji Process Hard plates. During the diffraction experiment the liquid sample reservoir has been cooled by a freezing mixture of ice and sodium chloride to reduce the amount of the sample vapor. The camera length was 11.82 cm. and the wave length of electron was 0.0578 Å, which was determined by measuring the transmission patterns of a gold foil.

Two pairs of photographs of the exposures of 25 and 50 sec., and of 30 and 60 sec. were used for intensity measurement. The optical densities of these plates were measured by the microphotometer. The photographic plates were rotated rapidly around the center of the diffraction pattern while being scanned by the microphotometer.

Analysis

Optical densities of each pair of the diffraction photographs were converted to relative intensity by Karle's procedure[9]. A smooth background line was drawn through the intensity curve multiplied by q and molecular intensity curve $M(q)$ was obtained by the following formula

$$M(q)=(I_{\mathrm{T}}-I_{\mathrm{B}})/I_{\mathrm{B}}, \qquad (1)$$

where I_{T} is the total intensity and I_{B} is the background intensity.

Radial Distribution Curve. — The radial distribution carve was calculated from the molecular intensity curve $M(q)$ according to the following equation:

$$f(r)=\sum_{q=1}^{90} qM(q)\exp(-aq^2)\sin(\pi qr/10) \qquad (2)$$

where the value of a is chosen as 0.000284 to make the integrand of Eq. 2 converge rapidly and $q=(40/\lambda)\sin(\theta/2)$, where θ is the angle of scattering and λ is the wavelength of the electron beam. The intensity curve from $q=0$ to $q=18$ was spliced by the theoretical intensity curve calculated for an assumed model.

A few steps of successive approximation were made to get a reasonable background line which would satisfy Karle's criterion of non-negativeness in the radial distribution curve as closely as possible. The final molecular intensity curve is shown in Fig. 1 and the radial distribution curve in Fig. 2.

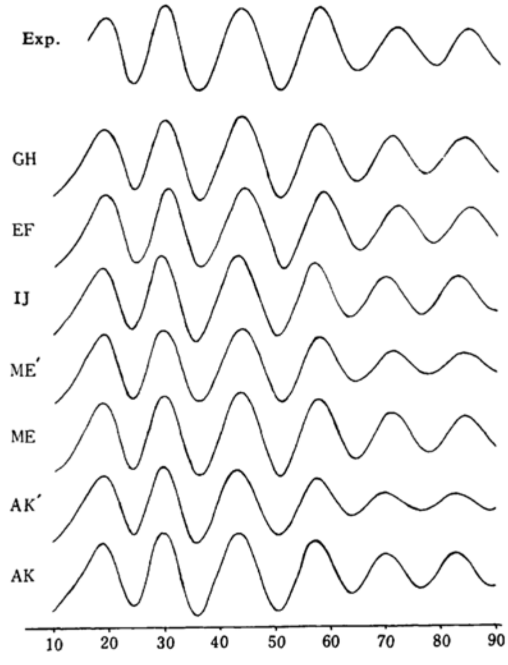


Fig. 1. Experimental and theoretical intensity curves.

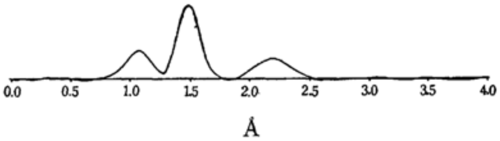
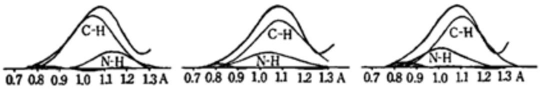


Fig. 2. The radial distribution curve.



A B C

Fig. 3. Analysis of the first peak of the radial distribution curve.

TABLE II. ANALYSIS OF THE FIRST PEAK OF RADIAL DISTRIBUTION CURVE

Set	Atomic pair	Equilibrium distance, Å	Mean amplitude, Å
A	C-H	1.05	0.065
	N-H	1.14	0.03
B	C-H	1.09	0.075
	N-H	1.04	0.07
C	C-H	1.11	0.06
	N-H	1.01	0.04

The radial distribution curve consists of three peaks at about 1.09 Å, 1.49 Å and 2.19 Å. The first peak is due to bonded C-H and N-H distances, the second to bonded C-C and C-N distances and the third to non-bonded N···cH, C···cH and C···nH distances. It is difficult to separate the first and the second peaks into two components and the third into three components respectively, because these component peaks overlap each other heavily. The first peak can be resolved into its components by three distinct sets of parameters (Fig. 3 and Table II). Sets A and C are the extreme cases for the differences between C-H and N-H

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[9] J. Karle and I. L. Karle, *J. Chem. Phys.*, **18**, 957, 963 (1950).

D E F

Fig. 4. Analysis of the second peak of the radial distribution curve.

TABLE III. ANALYSIS OF THE SECOND PEAK OF RADIAL DISTRIBUTION CURVE

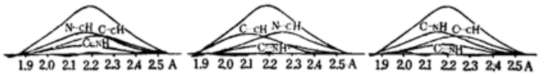
Set	Atomic pair	Equilibrium distance, Å	Mean amplitude, Å
D	C-N	1.51	0.02
	C-C	1.42	0.02
E	C-N	1.49	0.05
	C-C	1.48	0.05
F	C-N	1.47	0.03
	C-C	1.54	0·03

equilibrium distances. So the reasonable ranges of equilibrium distances are C-H=1.05~1.11 Å and N-H=1.01~1.14 Å.

The second peak can also be resolved into two component peaks by three distinct sets of parameters (Fig. 4 and Table III).

Sets D and F are the extreme cases for the differences between C-N and C-C equilibrium distances. There is an intimate relation between the difference of atomic distances and their mean amplitudes, that is when the difference becomes larger, the assumed mean amplitudes must be smaller in order to explain the peak of radial distribution curve well. This relation shall be discussed once more later at the correlation method. Here the reasonable equilibrium distances are thought to be C-N=1.47~1.51 Å and C-C=1.42~1.54 Å.

The third peak is the lowest among the three and consists of three component peaks of non-bonded C···cH, N···cH and C···nH. Therefore there may be many reasonable sets of resolution into its components. Some probable examples are listed in Fig. 5 and Table IV. In set G the atomic distances are equivalent to ∠CCH$_2$=160°, ∠HCH=117° and ∠C$_2$NH=122°, assuming C-C=1.48 Å, C-N=1.49 Å, C-H=1.08 Å and N-H=1.04 Å. In set H they are equivalent to ∠CCH$_2$=130°, ∠HCH=117° and ∠C$_2$NH=126° and in set I to ∠CCH$_2$=170°, ∠HCH=117° and ∠C$_2$NH=125°. Other sets of resolution show different atomic distances, so different bond angles. But by several attempts of resolution, the values ∠HCH≈117° and ∠C$_2$NH=120~130° seem to be probable. When N···cH distances become longer, C···cH distances become shorter and vice versa, assuming the bonded distances are constant, and at that time a reasonable resolution of the peak is obtained, so ∠CCH$_2$ can not be determined more accurately than the range 130~170°.



G H I

Fig. 5. Analysis of the third peak of the radial distribution curve.

TABLE IV. ANALYSIS OF THE THIRD PEAK OF RADIAL DISTRIBUTION CURVE

Set	Atomic pair	Equilibrium distance, Å	Mean amplitude, Å
G	C···cH	2.22	0.12
	C···nH	2.16	0.12
	N···cH	2.17	0.12
H	C···cH	2.11	0.11
	C···nH	2.21	0.11
	N···cH	2.25	0.11
I	C···cH	2.24	0.11
	C···nH	2.20	0.11
	N···cH	2.16	0.11

Correlation Method.—The theoretical intensity curves were calculated using the following equation:

$$qM(q)=\sum_{i,j}Z_iZ_j/r_{ij}\exp(-b_{ij}q^2)\sin(\pi q r_{ij}/10) \tag{3}$$

where r_{ij} is the equilibrium distance between atoms i and j and Z_i is the atomic number of atom i, apart from the value 1.25 for the hydrogen atom. The constant b_{ij} is equal to $(\langle \Delta r_{ij}^2\rangle/2)(\pi/10)^2$, where $\langle \Delta r_{ij}^2\rangle$ is the mean square amplitude of the atomic pair i and j.

Making reference to the results of radial distribution curve, various molecular models were selected for the theoretical intensity curves. At first in order to determine the acceptable C-C and C-N nuclear distances, theoretical intensity curves were drawn for the models in which both distances were varied in and out of the range found by the analysis of the second peak of radial distribution curve, assuming C-H=1.08 Å, N-H=1.04 Å, ∠CCH$_2$=160° and ∠C$_2$NH=120°. In Table V the constants of the models which were examined and mean values and average deviations of $q_{\text{calcd}}/q_{\text{obs}}$ were listed. In Fig. 1 some of the intensity curves were drawn. The features of the theoretical intensity curves of these models resembled each other, so the $q_{\text{calcd}}/q_{\text{obs}}$ ratios were used to select reasonable models.

If the mean amplitudes of both C-C and C-N are assumed to be 0.05 Å, which is nearly equal to those of the normal single bonds in most cases, the most reasonable model is such

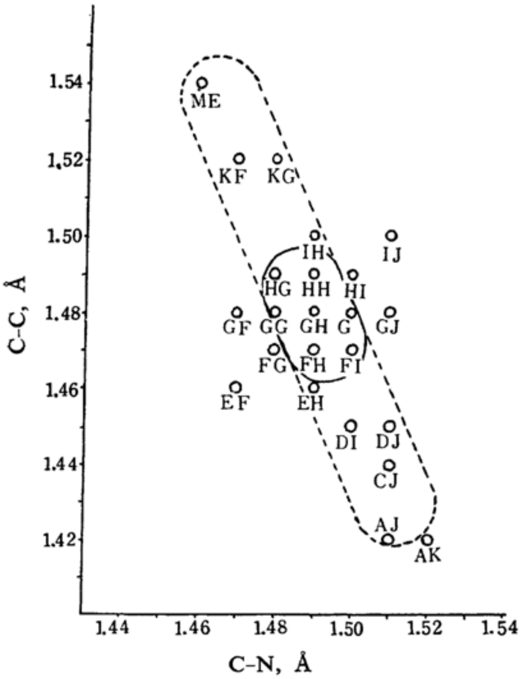


Fig. 6. The parameter chart. The area surrounded by a solid line is an acceptable region when the mean amplitudes are assumed to be 0.05Å, and the area surrounded by a broken line includes an acceptable region when the smaller mean amplitudes than 0.05Å are assumed.

that the C–C equilibrium distance is 1.48 Å and the C–N equilibrium distances are 1.49 Å. When C–N distances become longer than 1.49 Å, the acceptable model is such that the C–C distance becomes shorter than 1.48 Å and at that time the mean amplitudes of the atomic pairs should be smaller than 0.05 Å. If we fix the mean amplitudes as 0.05 Å, then in the case when the difference between C–N and C–C distances becomes larger, the amplitudes of the theoretical intensity curve become smaller at large q values compared to the experimental intensity curve, as the curve ME′ and AK′ in Fig. 1. So there is an intimate relation between the difference of the two distances and their mean amplitudes. From Fig. 6 and Table V reasonable C–C and C–N distances and acceptable regions of uncertainty are concluded as follows;

$$\text{C–C}=(1.48\pm 2d)\pm 0.02\ \text{Å}$$

$$\text{C–N}=(1.49\mp d)\pm 0.01\ \text{Å}$$

The parameter d is dependent upon the assumed mean amplitudes, M. A., of the atomic pairs. There is the following rough relation between them;

$$d=0.05-\text{M.A.}$$

TABLE V. LIST OF MEAN VALUES OF $q_{\text{calcd}}/q_{\text{obs}}$ AND THEIR AVERAGE DEVIATIONS WHEN C–C AND C–N DISTANCES WERE VARIED, ASSUMING THE OTHER PARAMETERS TO BE CONSTANT

Model	C–C Å	C–N Å	Mean amplitude	Mean value of $q_{\text{calcd}}/q_{\text{obs}}$	Average deviation of $q_{\text{calcd}}/q_{\text{obs}}$
GH	1.48	1.49	0.05	1.000	0.004
GG	1.48	1.48	0.05	1.004	0.006
GI	1.48	1.50	0.05	0.995	0.005
GF	1.48	1.47	0.05	1.008	0.004
GJ	1.48	1.51	0.05	0.990	0.006
FH	1.47	1.49	0.05	1.001	0.006
HH	1.49	1.49	0.05	0.997	0.007
EH	1.46	1.49	0.05	1.003	0.006
IH	1.50	1.49	0.05	0.993	0.006
FG	1.47	1.48	0.05	1.006	0.005
FI	1.47	1.50	0.05	0.997	0.006
HG	1.49	1.48	0.05	1.001	0.006
HI	1.49	1.50	0.05	0.993	0.007
EF	1.46	1.47	0.05	1.013	0.005
IF	1.50	1.47	0.05	1.004	0.005
IJ	1.50	1.51	0.05	0.986	0.006
EJ	1.46	1.51	0.04	0.994	0.007
DI	1.45	1.50	0.04	0.999	0.007
KF	1.52	1.47	0.04	1.001	0.004
KG	1.52	1.48	0.04	0.996	0.007
DJ	1.45	1.51	0.03	0.996	0.008
CJ	1.44	1.51	0.03	0.996	0.006
KE	1.52	1.46	0.03	1.006	0.004
ME	1.54	1.46	0.03	1.003	0.004
ME′	1.54	1.46	0.05	1.003	0.004
AJ	1.42	1.51	0.02	0.998	0.008
AK	1.42	1.52	0.02	0.993	0.007
AK′	1.42	1.52	0.05	0.993	0.009

Next C–H and N–H bond distances were investigated. There are similar relations among C–H and N–H bond distances and their mean amplitudes as in the case of C–C and C–N distances. But as the contributions of the former ones to the intensity curves are smaller than those of the latter ones, the above relation is somewhat obscure. The mean values of $q_{\text{calcd}}/q_{\text{obs}}$ and their average deviations for the models in which C–H and N–H distances have been varied, are represented in Table VI. Reasonable ranges of C–H and N–H distances are 1.05∼1.11 Å and 1.00∼1.11 Å, respectively.

Finally the angles HCH, CCH_2 and C_2NH were investigated. When ∠HCH is varied from 109.5° to 130°, the $q_{\text{calcd}}/q_{\text{obs}}$ values change but slightly (Table VII). The model of 117° seems to be the best, but the above range of angles will be within the experimental error. When the angles CCH_2 increase, C···cH distances increase and N···cH distances decrease, consequently the $q_{\text{calcd}}/q_{\text{obs}}$ values remain

TABLE VI. LIST OF MEAN VALUES OF $q_{\text{calcd}}/q_{\text{obs}}$ AND THEIR AVERAGE DEVIATIONS WHEN C-H AND N-H DISTANCES WERE VARIED, ASSUMING THE OTHER PARAMETERS TO BE EQUAL TO MODEL GH

Model	C–H Å	C–N Å	Mean amplitude	Mean value of $q_{\text{calcd}}/q_{\text{obs}}$	Average deviation of $q_{\text{calcd}}/q_{\text{obs}}$
MO	1.08	1.00	0.075	1.000	0.004
GH	1.08	1.04	0.075	1.000	0.004
MN	1.08	1.12	0.075	0.998	0.004
LP	1.05	1.04	0.075	1.000	0.005
LN	1.05	1.12	0.06	0.999	0.006
NP	1.12	1.04	0.06	0.997	0.004
ON	1.12	1.00	0.06	0.998	0.006

TABLE VII. LIST OF MEAN VALUES OF $q_{\text{calcd}}/q_{\text{obs}}$ AND THEIR AVERAGE DEVIATIONS WHEN THE ANGLES HCH WERE VARIED, ASSUMING THE OTHER PARAMETERS TO BE EQUAL TO MODEL GH

Model	∠HCH	Mean value of $q_{\text{calcd}}/q_{\text{obs}}$	Average deviation of $q_{\text{calcd}}/q_{\text{obs}}$
Q	109.5°	0.999	0.005
GH	117°	1.000	0.004
R	130°	1.000	0.006

TABLE VIII. LIST OF MEAN VALUES OF $q_{\text{calcd}}/q_{\text{obs}}$ AND THEIR AVERAGE DEVIATIONS WHEN THE ANGLES CCH_2 WERE VARIED, ASSUMING THE OTHER PARAMETERS TO BE EQUAL TO MODEL GH

Model	$\angle CCH_2$	Mean value of $q_{\text{calcd}}/q_{\text{obs}}$	Average deviation of $q_{\text{calcd}}/q_{\text{obs}}$
S	130°	0.999	0.005
T	140°	0.999	0.005
U	150°	0.999	0.005
GH	160°	1.000	0.004
V	170°	1.000	0.005

TABLE IX. LIST OF MEAN VALUES OF $q_{\text{calcd}}/q_{\text{obs}}$ AND THEIR AVERAGE DEVIATIONS WHEN THE ANGLE C_2NH WAS VARIED, ASSUMING THE OTHER PARAMETERS TO BE EQUAL TO MODEL GH

Model	$\angle C_2NH$	Mean value of $q_{\text{calcd}}/q_{\text{obs}}$	Average deviation of $q_{\text{calcd}}/q_{\text{obs}}$
W	90°	0.999	0.006
GH	120°	1.000	0.004
Y	180°	0.998	0.005

almost unchanged (Table VIII). So the angles CCH_2 may be determined only in the range 130∼170°, as having been mentioned in the radial distribution analysis. As the contribution of C···NH atomic pairs to the total molecular intensity curve is the smallest except that of H···H atomic pairs which is negligibly small in this case, and their distances are comparable to those of C···CH and N···CH, the angle C_2NH can not be determined unambiguously. But from the $q_{\text{calcd}}/q_{\text{obs}}$ values (Table IX), the reasonable value seems to be about 120°.

Summary and Discussion

By the radial distribution and correlation methods, the molecular structure of ethylenimine was obtained as follows;

$$\text{C–C} = (1.48 \pm 2d) \pm 0.02\,\text{Å}$$

$$\text{C–N} = (1.49 \mp d) \pm 0.01\,\text{Å}$$

where

$$d = 0.05 - \text{M.A.}$$

$$\text{C–H} = 1.08 \pm 0.03\,\text{Å},\quad \text{N–H} = 1.05 \pm 0.07\,\text{Å}$$

The angles CCH_2 could not be determined accurately. They seem to be in the range 130∼170°. The angles HCH and C_2NH also could not be determined unambiguously, but $\angle HCH \approx 117°$ and $\angle C_2NH \approx 120°$ seem to be probable.

The above values of C–C and C–N nuclear distances are consistent with the values obtained by microwave spectroscopy (Table I). They are especially consistent when their mean amplitudes are assumed to be 0.05 Å.

As for the N–H bond distance and the angle C_2NH, the present values coincide with those of microwave spectroscopy within the extents of uncertainty, but the most probable values of the former are somewhat larger than the latter.

The C–C distance 1.48 Å is considerably shorter than the single bond distance 1.54 Å of normal chain compounds as the other three-membered ring compounds.

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