An Electron Diffraction Investigation on the Molecular Structure of Hydrazine

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The molecular structure of hydrazine was studied in 1943 by Giguére and Schomaker[1] with the visual method of electron diffraction and the N–N distance was found to be 1.47±0.02 Å. Recently Yamaguchi et al.[2] in this Department studied the infrared vibration-rotation spectrum of the molecule and recognized a difficulty in interpreting the spectrum by the use of this distance. Strictly speaking, the moment of inertia can not be fixed uniquely by the vibration-rotation spectrum alone, for there is a wide choice in selecting the J and K numbering without any other information. Thus, precise determination of the N–N distance was desirable for the proper assignment of the spectral lines. The principal object of the research is to determine the N–N distance as accurately as possible by the sector-microphotometer method, and, if possible, to measure the root mean square amplitudes of thermal vibration.

Experimental

The sample of hydrazine was kindly provided by Dr. Yamaguchi. The apparatus for electron diffraction was the same as that reported in the preceding paper[3]. An r^3-sector was used. The camera length was 11.82 cm. and the accelerating voltage used was about 45 kV. The nozzle was heated to about 60°C and the sample holder to about 30°C. The measured range was from 17 to 100 in q-unit. The diffraction patterns were traced on a Rigaku-Denki MP-3 microphotometer. During the tracing the photographic plates were rotated rapidly about the center of the diffraction pattern.

Structure Analysis

Karle's method[4] was applied to a pair of photographs of different exposure (1 : 1.5). The density-intensity calibration curve was found to be linear in the whole range of the measurement. The ratio of density between the two photographs was consistent with the ratio of the time of exposure.

The molecular intensity curves, $qM(q)$, were obtained by the procedure developed by Karle and Karle. The result is shown in Fig. 1. The radial distribution curve (Fig. 2) was calculated by the Fourier transformation of the observed molecular intensity multiplied by an artificial factor $\exp(-bq^2)$ with $b=0.0002303$, which was assumed so as to reduce the intensity to one tenth of the original at $q=100$. In order to diminish the effect of series termination, the observed intensity curve was spliced with a curve calculated for an assumed model, below 20 and from 90

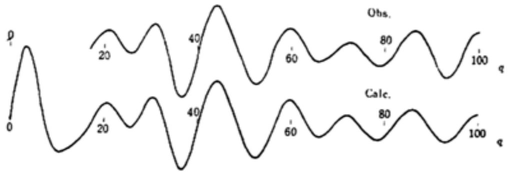

Fig. 1. Observed and calculated molecular intensity curves, $qM(q)$, of hydrazine.

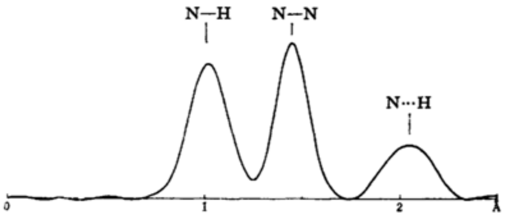

Fig. 2. The modified radial distribution curve of hydrazine.

TABLE I. MOLECULAR PARAMETER OF THE MODEL ASSUMED FIRST FOR THE CALCULATION OF THE SUPPLEMENTARY PART OF THE RADIAL DISTRIBUTION CURVE

	Atomic distance	Root mean square amplitude
N–N	1.47 Å	0.052 Å
N–H	1.04 Å	0.074 Å
N···H	2.05 Å	0.100 Å

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[1] P. A. Giguére and V. Schomaker, *J. Am. Chem. Soc.*, **65**, 2025 (1943).

[2] A. Yamaguchi, I. Ichishima, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **31**, 843 (1959).

[3] Y. Morino and K. Kuchitsu, ibid., **28**, 175 (1958).

[4] J. Karle and I. Karle, ibid., **27**, 1052 (1949); **18**, 957 (1950).

to 120 in q-scale. The molecular parameters of the starting model are given in Table I. The equilibrium distances were taken from the paper of Giguére and Schomaker. For the mean amplitude of N–N, that of C–O pair in methanol, 0.052 Å, was adopted. The mean amplitude for the pair of N–H, 0.074 Å, was calculated with an N–H diatomic molcule having the frequency of the symmetric stretching vibration of NH_3, 3337 cm^{-1}. Finally, for the pair of non-bonded N···H the observed value of a C···H pair in n-butane, 0.100 Å, was used. The model was refined by successive approximation. The calculations of the molecular intensity curve and of the radial distribution curve were performed with the aid of a parametron computer PC–1.

The index of resolution was found to be about 95%. Each peak of the radial distribution curve was fitted with a Gaussian in shape to obtain $r_m(f)$ from the position of the maximum of the Gaussian peak, and $<\Delta r^2>^{1/2}$ from the width of the peak. The failure of Born approximation was corrected by Bartell-Brockway method[5]. Using the values of $r_m(f)$, $<\Delta r^2>^{1/2}$, and the index of resolution, thus obtained, the theoretical intensity curve was computed. It is compared with the observed in Fig. 1. Agreement is very well up to 90 in q-scale. The final values of the molecular constants listed in Table II were established by taking average over the values obtained by four photographs.

TABLE II. FINAL OBSERVED VALUES OF ATOMIC DISTANCES AND THEIR MEAN SQUARE AMPLITUDES

	$r_m(f)$	$<\Delta r^2>^{1/2}$	r_0 (spectroscopic)[2]
N–N	1.449 ±0.004 Å	0.051 ±0.005 Å	1.453 ±0.005 Å
N–H	1.022 ±0.006 Å	0.074 ±0.007 Å	1.025 ±1.020 Å
N···H	2.063 ±0.015 Å	0.103 ±0.015 Å	—
N–N–H	112.0 ±1.5°	—	112 ~112.5°

Calculation of Mean Amplitudes

As was shown by one of the present author[6], the mean square amplitude of a distance between a pair of atoms is given by

$$<\Delta R_i^2> = \sum_k L_{ik}^2 <Q_k^2>$$

where $<Q_k^2>$ is the mean spuare amplitude of the k-th normal vibration and is given by the normal frequency as follows:

$$<Q_k^2> = \frac{h}{8\pi^2\nu_k} \coth \frac{h\nu_k}{2kT}$$

L_{ik} is the element of the $\boldsymbol{L}$ matrix which transforms the internal coordinates to the normal coordinates. $L_{ik}^2<Q_k^2>$ indicates the contribution of the k-th normal vibration to the mean square amplitude of R_i.

The $\boldsymbol{L}$ matrix elements of the hydrazine molecule were calculated by Yamaguchi by the use of the frequencies of the normal vibrations obtained by the Raman and infrared spectra. The temperature of the sample was estimated to be 333°K. The calculated values are shown in Table III, with a reference to the observed values.

TABLE III. CALCULATED VALUES OF MEAN SQUARE AMPLITUDES IN THE UNIT OF 10^{-4} Å^2

	Frequency (cm^{-1})	Designation	N–N	N–H	N···H
A	3280	N–H sym. stretching	0.1	15.0	7.2
	3325	N–H antisym. stretching	0.0	12.1	5.6
	1587	bending	1.4	0.0	3.5
	1275	twisting	0.0	0.0	20.9
	1098	N–N stretching	19.7	0.1	12.7
	780	wagging	0.6	0.0	3.1
	377	torsion	0.0	0.0	0.0
B	3314	N–H sym. stretching	—	10.5	7.3
	3350	N–H antisym. stretching	—	16.3	9.1
	1628	bending	—	0.2	6.2
	1275	twisting	—	0.0	11.4
	966 933	wagging	—	0.0	10.4
Total			21.8	54.2	97.4
Observed mean square amplitude			26	55	106

Discussion

The N–N bond distance was found to be 1.449±0.004 Å. It is apparently smaller than that by Giguére and Schomaker, 1.47 Å, although the difference is of the same order of magnitude as the error of their value. The final assignment of the spectral lines of the infrared spectrum provided 1.453±0.005 Å[2], in good agreement with the value newly obtained. The N–H distance and the angle of N–N–H obtained by both methods are compared in Table II. For the infrared spectrum, it is the moment of inertia that gives the spacings of the spectral lines, and the

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5) L. S. Bartell and L. O. Brockway, *Nature*, **171**, 978 (1953).

6) Y. Morino, K. Kuchitsu and T. Shimanouchi, *J. Chem. Phys.*, **20**, 726 (1952); Y. Morino, K. Kuchitsu, A. Takahashi and K. Maeda, *J. Chem. Phys.*, **21**, 1927 (1953).

moment of inertia strongly depends upon the position of the hydrogen atoms which are located at both ends of the molecule. Hence the N–H distance and the N–N–H bond angle may be obtained more accurately by the infrared spectrum. It must be admitted that the non-bonded N···H distance might contain a fairly large error in the electron diffraction measurement, because the halos in the inner region (<17 in q-scale) have not been measured. In fact, the N···H peak in the radial distribution curve was found to be appreciably deformed from the Gaussian.

For the mean square amplitudes, the agreement between the observed and the calculated is quite satisfactory, as shown in Table III. Large systematic errors would be contained in the observed values, because the effects of non-nuclear scattering and of finite sample size were not corrected for the observed values. It would be of interest to note that the contribution of the N–N stretching mode to the mean amplitude of N–N pair and that of the N–H stretching modes to the bonded N–H mean amplitude are the most predominant, whereas for the non-bonded N···H pair many modes contribute in comparable order of magnitude.

Summary

By the sector-microphotometer method of electron diffraction the molecular structure of hydrazine was obtained as shown in Table II. The bond distances are in good agreement with the values obtained by the infrared vibration-rotation spectrum. The mean amplitudes agreed with the calculated values within the limits of errors.

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