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MOLECULAR STRUCTURE AND CONFORMATION OF 1,2-DIMETHYLHYDRAZINE STUDIED BY GAS ELECTRON DIFFRACTION

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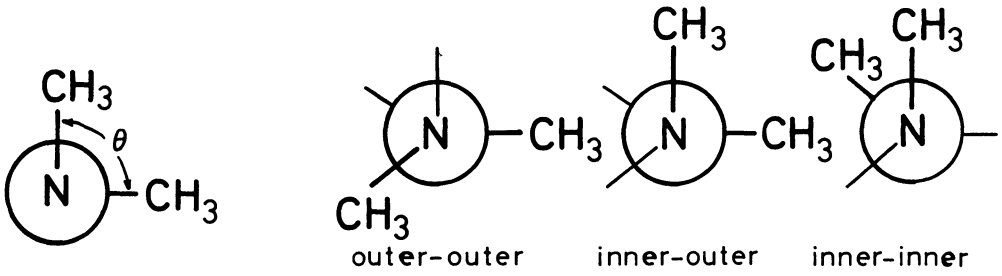
An electron diffraction study has shown that the inner-outer conformer of 1,2-dimethylhydrazine, the C-N-N-C dihedral angle being estimated to be about 90°, is a major conformer in the gas phase. Another conformer is found to have a smaller dihedral angle (inner-inner form). The thermal-average bond distances and angles of the inner-outer conformer have been determined.

The rotational isomerism about the N-N axis in 1,2-dimethylhydrazine has been investigated by the measurement of thermodynamic properties,[1] infrared and Raman spectroscopy,[2] and photoelectron spectroscopy.[3] The molecule was found to exist in more than one conformer in the liquid and gas phases, but no definitive assignment of the conformers has yet been reported. Possible conformers are three gauche (outer-outer, inner-outer, and inner-inner, as shown in Fig. 1), cis, and trans forms.[1-3] The infrared and Raman studies[2] suggested that the molecule in the liquid phase was a mixture of the gauche forms (either outer-outer and inner-inner or inner-outer and inner-inner) instead of the trans form. According to the analysis of photoelectron spectra by the use of CNDO/2 calculations,[3] the observed nonbonding splitting indicated the existence of the inner-outer and/or inner-inner conformers, while the latter conformer was disfavored because an appreciable steric interaction of the two methyl groups was expected. The present study reports on the composition of the mixture of conformers and the geometrical structure of a major conformer determined by gas electron diffraction.

Fig. 1. Possible conformers of 1,2-dimethylhydrazine, $CH_3NHNHCH_3$, as viewed along its N-N axis.



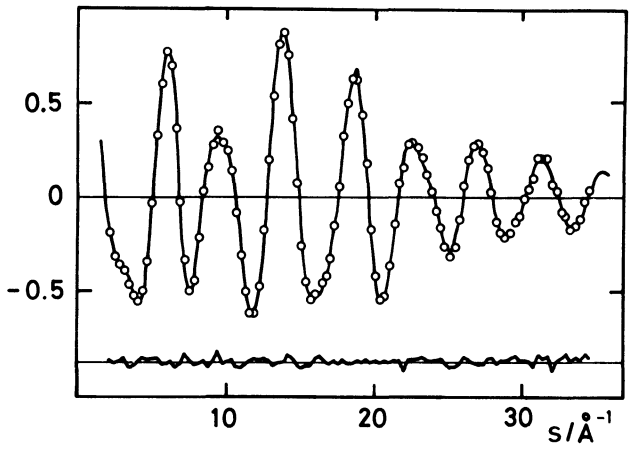


Fig. 2. Experimental and theoretical molecular intensities for dimethylhydrazine. Typical observed sM(s) values are shown as open circles. The solid curve represents the best fit theoretical intensities. The difference between the observed and theoretical curves is also shown.

The sample of 1,2-dimethylhydrazine was obtained by neutralization of its dihydrochloride (purchased from K & K Inc.) with sodium hydroxide. Diffraction photographs were taken at two camera distances (about 10.8 and 24.3 cm) with 40 keV electrons, the energy constancy being within 0.01%.[4,5] The vapor pressure of the sample, which was maintained in thermal equilibrium with its liquid phase at 30°C, was about 60 Torr. The molecular intensity obtained by a standard procedure[6] in the range of s=3.1-32.1 Å^{-1} (Fig. 2) was analyzed. Most of the calculations were carried out on a HITAC 8800/8700 in the Computer Center of the University of Tokyo.

Trial analyses of the molecular intensity and the radial distribution curve showed that a majority of the molecule had a conformation with the C-N-N-C dihedral angle of about 90°. This angle corresponds to the inner-outer conformer. A part of the radial distribution curve calculated for this conformer is illustrated in Fig. 3(a). The difference between the observed and calculated curves indicates the existence of an inner-inner conformer, whose dihedral angle is smaller than that of the inner-outer conformer. Least-squares calculations were carried out to determine the structural parameters, including the dihedral angle for the inner-outer conformer. The relative abundance was treated as one of the variable parameters, whereas the dihedral angle of the inner-inner conformer was fixed, because there was a strong correlation between these parameters. The following additional assumptions were made on the frame structures of the conformers:

(1) All the structural parameters for the two conformers are equal to each other except for their dihedral angles.

(2) All the C-H bond lengths are equal. Two methyl groups have local C_{3v} symmetry and have no tilt.

(3) The methyl torsional angles are estimated by calculation of nonbonded interactions among the hydrogen atoms in such a way that the total energy takes a minimum. They are thus assumed to be 15° and -10° for the inner and outer methyl groups, respectively, as measured in the clockwise direction from the position in which one of the C-H bonds lies trans to the N-N bond.

(4) The N-N-H angles are equal to those in hydrazine: 111.2° for the inner and 106.5° for the outer positions.[7]

(5) The C-N-H angles are equal to that in methylhydrazine (103°).[7]

(6) The H-C-H angles are equal to those in methylhydrazine (107.8°).[7]

The mean amplitudes and the corrections (r_a-r_α)[8] for the shrinkage effects were calculated for the inner-outer conformer on the basis of the Urey-Bradley force field.[9] All the mean amplitudes were fixed at the calculated values in the subsequent analyses.

As a result, the correlation diagram shown in Fig. 4 was obtained. From this figure, the relative abundance of the inner-outer conformer was found to range between 85 and 46%, corresponding to the range of the dihedral angle of the inner-inner conformer, 20° to 50°. The analyses in which this dihedral angle was fixed to values outside this range gave larger standard deviations or no convergence. Therefore, it is highly probable that these parameters fall within the ranges given above and that the inner-outer conformer is dominant. The frame structure and the dihedral angle of the dominant conformer, listed in Table 1, were not substantially affected by this correlation; small differences in the most probable values originated from different assumptions were included in their estimated error limits.

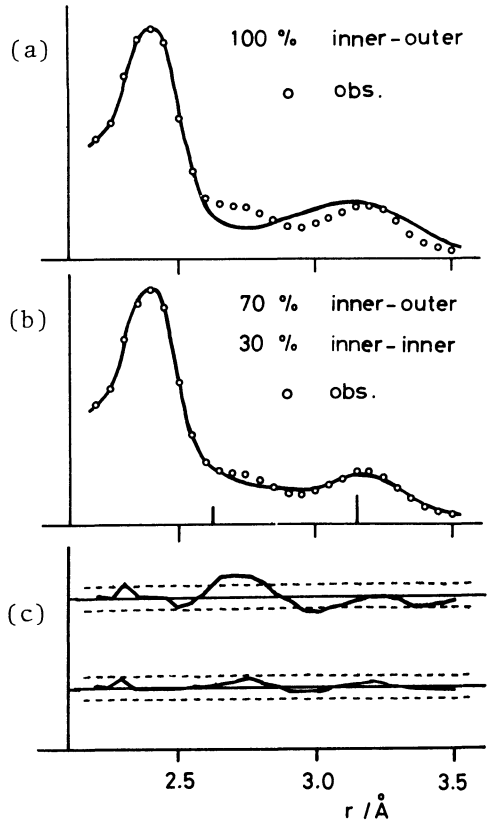


Fig. 3. Experimental and theoretical radial distribution curves for (a) 100% inner-outer and (b) a mixture of 70% inner-outer and 30% inner-inner conformers. Vertical bars ar r∿ 2.7 Å and 3.2 Å correspond to the distances between the two methyl carbon atoms for the inner-inner (θ=30°) and inner-outer (90°) conformers, respectively. (c) Residuals for (a) (upper) and (b) (lower). Broken lines denote the error limits estimated from reproducibility of the observed curves.

Table 1. Structural parameters for 1,2-dimethylhydrazine (in Å and degrees)

	r_α	r_g	ε[a]
r(N-H)	1.029	1.034	0.016
r(C-H)	1.113	1.119	0.012
r(N-N)	1.417	1.419	0.011
r(C-N)	1.461	1.463	0.005
∠N-N-C	112.0	——	1.0
θ[b]	90	——	12

a) Estimated limits of error.

b) The C-N-N-C dihedral angle of the inner-outer conformer.

Figure 3(b) shows a typical radial distribution curve based on a model with the dihedral angle and the relative abundance of the inner-inner conformer assumed to be 30° and 30%, respectively. This curve fits better with the observed curve than Fig. 3(a). In conclusion, the inner-outer and inner-inner conformers exist in the gas phase. This finding is consistent with one of the conformational models proposed by the infrared and Raman study[2] and also with one of the models favored by the photoelectron study.[3] In order to improve the accuracy of the relative abundance and the dihedral angle of the inner-inner conformer, the Raman spectra of this molecule in the liquid and gas phases are being studied.

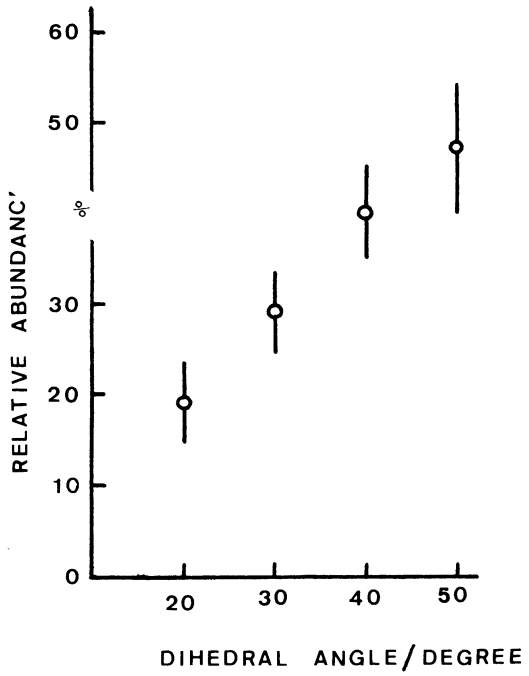


Fig. 4. Diagram showing the correlation between the abundance and the dihedral angle of the inner-inner conformer. Four independent least-squares analyses were carried out with the dihedral angle of the inner-inner conformer fixed at 20, 30, 40, and 50°. Vertical bars denote the error limits estimated from the standard deviations of the least-squares analyses.

References and Note

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9) Force constants were estimated from those for hydrazine and methylamine and then adjusted by trial and error calculations.

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