

An Electron Diffraction Study of Azomethane, CH_3NNCH_3

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The molecular structure of azomethane has been determined by electron diffraction. The most important molecular parameters are $R(\text{C}-\text{H}) = 1.105(3) \text{ \AA}$, $R(\text{N}=\text{N}) = 1.247(3) \text{ \AA}$, $R(\text{C}-\text{N}) = 1.482(2) \text{ \AA}$ and $\angle \text{C}-\text{N}=\text{N} = 112.3^\circ(0.3^\circ)$.

The molecular structure of azomethane has previously been determined by electron diffraction in 1935.¹ It was felt that the time had now come for a new and more accurate investigation.

EXPERIMENTAL AND CALCULATION PROCEDURE

Azomethane was synthesized from hydrazomethane-bis-hydrochloride as outlined by Thiele² and purified by vacuum distillation. The electron scattering pattern from the gas was recorded on the Oslo electron diffraction unit³ with a nozzle temperature of $15 \pm 5^\circ\text{C}$. Exposures were made at nozzle-to-photographic-plate distances of about 48 cm and 20 cm. Four apparently faultless plates from each set were photometered and processed in the usual way.⁴ The resulting modified molecular intensity points are shown in Fig. 1. They extend from $s = 2.00 \text{ \AA}^{-1}$ to $s = 38.00 \text{ \AA}^{-1}$, $s = (4\pi/\lambda) \sin(\theta/2)$ where λ is the electron wavelength and θ the diffraction angle. Below $s = 10.00 \text{ \AA}^{-1}$ the point density is eight points per \AA^{-1} , above 10.00 \AA^{-1} four points per \AA^{-1} .

Theoretical intensity curves were calculated from

$$I_{\text{CC}}(s) = \sum_{i \neq j} \frac{|f_i(s)| \cdot |f_j(s)|}{|f_{\text{C}}(s)|^2} \cos(\eta_i(s) - \eta_j(s)) \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\frac{1}{2}u_{ij}^2s^2)$$

$$= \sum_{i \neq j} g_{ij/\text{CC}}(s) \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\frac{1}{2}u_{ij}^2s^2)$$

The sum extends over all atom pairs i, j in the molecule. R_{ij} is the internuclear distance, u_{ij} the root mean square amplitude of vibration. $f_j(s) = |f_j(s)| \exp(i\eta_j(s))$ is the complex atomic scattering factor of atom j . It has been calculated for N, C, and H by the partial wave approximation with a program written by Peacher.⁵ The scattering potentials of nitrogen and carbon have been found by non-relativistic Hartree-Fock calculations.^{6,7}

Radial distribution curves were calculated by Fourier inversion of experimental or theoretical intensity curves after multiplication with the artificial damping function $\exp(-ks^2)$.

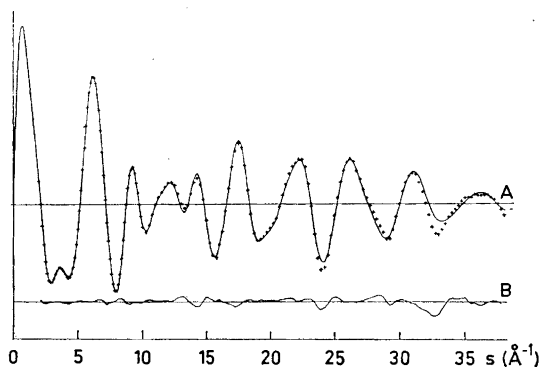


Fig. 1. A: Theoretical modified molecular intensity curve of azomethane with experimental values indicated by \times . B: Difference curve.

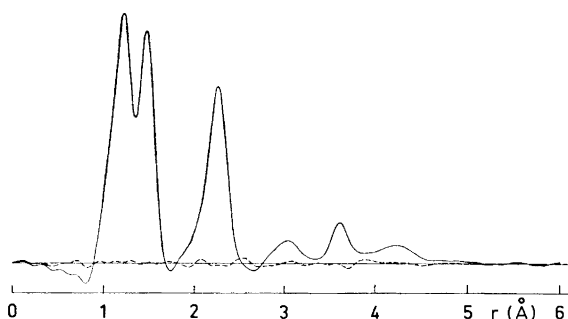


Fig. 2. Full line: Experimental radial distribution curve of azomethane. The artificial damping constant $K=0.002 \text{ \AA}^2$. Dashed line: Difference between experimental curve and a theoretical curve calculated for best model.

STRUCTURE ANALYSIS

An experimental radial distribution function is shown in Fig. 2. The peak at 1.11 \AA corresponds to the C–H bond distances, the peak at 1.48 \AA to the C–N bond distances. A peak at 1.25 \AA corresponding to the N=N double bond distance fills in the valley between them. The peak at 2.25 \AA is composite, the main contribution being a peak representing the C \cdots N non-bonded distance. The peak at 3.0 \AA arises from distances of type N1 \cdots H5 (see Fig. 3), the peak at 3.6 \AA from the C \cdots C non-bonded distance and the broad peak at 4.2 \AA from distances of type C1 \cdots H5.

The molecular structure was refined by least-squares calculations on the intensity data with a diagonal weight matrix.⁴ It was assumed that azomethane has the C_{2h} structure shown in Fig. 3. It was further assumed that the methyl groups have C_{3v} symmetry. The angle between the threefold axes and the

C–N bonds (the methyl group “tilt”) was refined as an independent parameter. The tilt angle was defined as positive when the hydrogen atoms are moved *away* from the double bond.

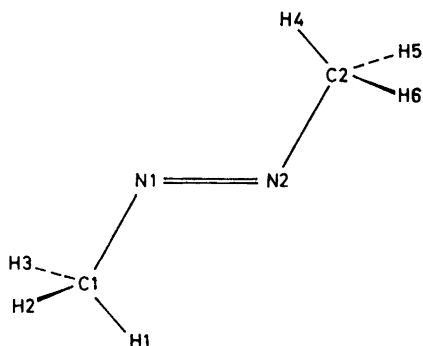


Fig. 2. Molecular model of azomethane.

In order to make the refinement converge it was necessary to assume that all C–H bond distances have the same vibrational amplitude, and that the $N1\cdots H1$ and $N1\cdots H2$ distances have identical amplitudes. In the final least-squares cycle, however, the two latter were treated as independent parameters. The $H\cdots H$ amplitude within a methyl group was fixed at 0.12 Å (the value found in methane⁸), all other $H\cdots H$ amplitudes were fixed at 0.20 Å; these amplitudes were not refined.

The final parameters and their estimated standard deviations are listed in Table 1. The standard deviations obtained by least-squares calculations have been multiplied by a factor of 2.0 for distances and angles and a factor of 3.0 for amplitudes to account for correlation in the intensity data,⁹ and further expanded to take into account an uncertainty of 1.4 ppt in the electron wavelength.¹⁰

Table 1. Structure parameters of azomethane with estimated standard deviations. The angles have not been corrected for shrinkage.

	R (Å)	u (Å)
C–H	1.105(3)	0.094(6)
C–N	1.482(2)	0.059(2)
N=N	1.247(3)	0.044(3)
C \cdots N	2.270(3)	0.070(10)
C \cdots C	3.625(4)	0.077(3)
N1 \cdots H1	2.04(11)	0.17(12)
N1 \cdots H2	2.12(4)	0.17(8)
N1 \cdots H4	2.21(15)	0.64(52)
N1 \cdots H5	2.99(2)	0.18(3)
C1 \cdots H4	3.69(14)	0.61(90)
C1 \cdots H5	4.25(3)	0.20(6)
\angle C–N=N	112.3°(0.3°)	
\angle N–C–H1	107.5°(1.5°)	
tilt	–4.1°(6.1°)	

DISCUSSION

After our study had been completed, we became aware of the fact that azomethane had been the subject of a simultaneous gas phase electron diffraction investigation by Chang, Porter and Bauer.¹¹ The values obtained for the principal parameters by this group and their estimated standard deviations are¹²

	R (Å)	u (Å)
C—H	1.107(6)	0.081(5)
C—N	1.474(2)	0.062(2)
N=N	1.254(2)	0.046(2)
\angle C—N=N	111.9°(0.5°).	

The agreement between the two studies is not altogether satisfactory: the difference between the two estimates for the C—N bond distance is rather large compared to the estimated standard deviations.

The molecular structure of azobenzene has been determined by means of X-ray diffraction.¹³ The asymmetric unit contains two molecules, one of which is disordered. In the other molecule C—N=1.434(3) Å, N=N=1.247(3) Å, and \angle C—N=N=113.6°(0.3°).

That the C—N bond distance is about 0.05 Å less in azobenzene than in azomethane is not surprising: Firstly the covalent radius of carbon is assumed to decrease by about 0.03 Å on going from sp^3 to sp^2 hybridization. Secondly the C—N bond may have some π -character in the not far from planar azobenzene molecule.

The C—N=N valence angle is significantly different from 120° in both compounds. In fact the smallness of this single angle appears to be a characteristic feature for a large number of molecules containing the C—N=N grouping. The simplest explanation for this may be that the lowest energy of the molecule is obtained with the non-bonding electrons in an atomic orbital of considerable s -character.

This view receives support from the crystal structure of the complex of azomethane with cuprous chloride.¹⁴ In the complex each nitrogen atom appears to form a dative σ -bond with one copper atom which is lying in the plane of the azomethane molecule. The Cu—N=N angle is 125.4°(1.2°) and the Cu—N bond distance is 1.993(6) Å. The precision of the structure determination is not sufficient to show any change in bond distances from the free azomethane molecule, but the C—N=N valence angle has increased to 118.0°(1.6°). It seems reasonable to assume that the p -character of the lone pair orbital has been increased in order to give better overlap with orbitals on the copper atom.

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