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Bond Distances of Cyanogen as Determined by Gas Electron Diffraction

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The internuclear distances of cyanogen were determined by gas electron diffraction to be $r_g(\mathrm{C{\equiv}N}) = 1.163_4 \pm 0.001_9$ Å and $r_g(\mathrm{C{-}C}) = 1.392_5 \pm 0.002_2$ Å. The average moment of inertia calculated from this structure agreed with Maki's infrared results as corrected for rotation-vibration interaction. The spectroscopic moment of inertia obtained by Maki was used for calibrating the electron-diffraction scale factor, and the zero-point average distances, with their limits of error, were obtained as $r_z(\mathrm{C{\equiv}N}) = 1.155_2 \pm 0.001_3$ Å and $r_z(\mathrm{C{-}C}) = 1.387_1 \pm 0.001_4$ Å.

It has long been known that the length of a CC single bond depends on its environment. A carbon-carbon single bond adjacent to multiple bonds is found to be appreciably shorter than one in normal hydrocarbons, and the shortening is most conspicuous when the single bond is located between triple bonds.1) Cyanogen, C_2N_2, is one of the simplest molecules of this category. Earlier electron-diffraction measurements of this molecule by Pauling, Springall and Palmer2) and by Langseth and Mφller3) gave $r(\mathrm{C{\equiv}N}) = 1.16 \pm 0.02$ and 1.15 ± 0.02 Å, and $r(\mathrm{C{-}C}) = 1.37 \pm 0.02$ and 1.38 ± 0.02 Å, respectively. The precise rotational constants, B_0, for two isotopic species, $^{12}C_2{}^{14}N_2$ and $^{12}C_2{}^{15}N_2$, have been obtained by Maki4) from his rotational analysis of the infrared spectra. The resulting bond distances are $r_0(\mathrm{C{\equiv}N}) = 1.15_4 \pm 0.017$ Å and $r_0(\mathrm{C{-}C}) = 1.38_9 \pm 0.030$ Å.

On the basis of more recent developments in experiment and theory, a reliable average structure can be determined by the use of a combination of rotational constants obtained from high-resolution spectroscopy and internuclear distances obtained from electron diffraction.5) The present study aims to apply this method to determining the average structure of cyanogen in the ground vibrational state.

Experimental

A sample of cyanogen, which contained 0.6% carbon dioxide and 0.4% air, was kindly offered by Dr. Shizuo Nakamura of the Sagami Chemical Research Center. It was purified before use by pumping off any impurities from the sample while it was held at dry ice temperature.

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1) G. Herzberg, F. Patat and H. Verleger, *J. Phys. Chem.*, **41**, 123 (1937).

2) L. Pauling, H. D. Springall and K. J. Palmer, *J. Am. Chem. Soc.*, **61**, 927 (1939).

3) A. Langseth and C. K. Mφller, *Acta Chem. Scand.*, **4**, 725 (1950).

4) A. G. Maki, *J. Chem. Phys.*, **43**, 3193 (1965).

5) K. Kuchitsu and S. Konaka, *ibid.*, **45**, 4342 (1966); K. Kuchitsu, T. Fukuyama and Y. Morino, *J. Mol. Structure*, **1**, 463 (1968).

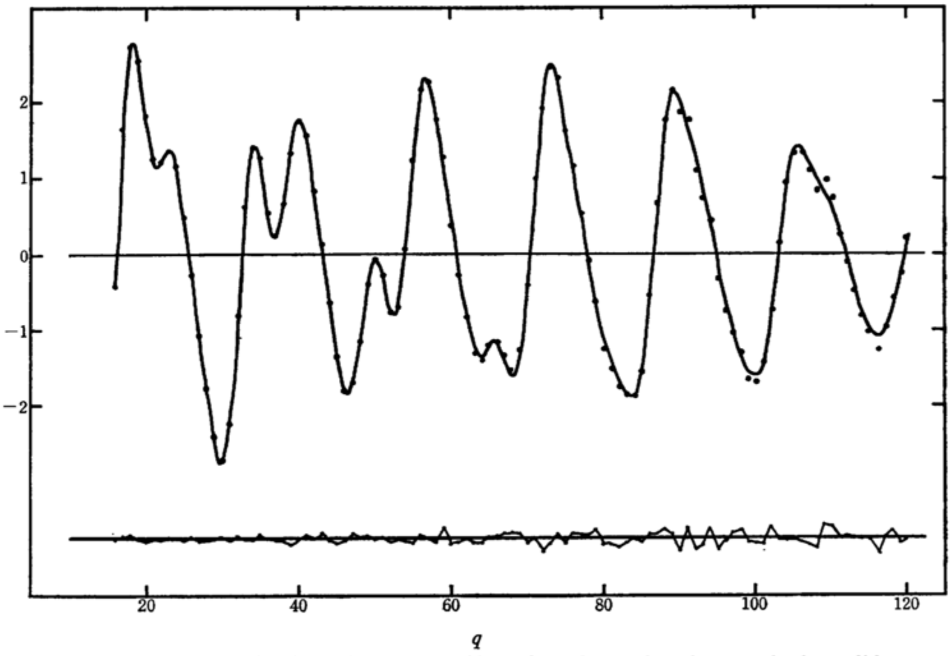

Fig. 1. Reduced molecular intensity curves (dots for observed values and the solid curve calculated from the best-fit model) and the residuals (below).

A diffraction apparatus with an r^3-sector previously reported⁵⁾ was used for the present study. The camera distances were measured as 243.22±0.02 and 107.78±0.02 mm. The accelerating voltage (about 40 kV) was stabilized within 0.1%. The wavelength of the electron beam was calibrated to 0.15% with reference to the r_a(C=O) bond distance (1.164_6 Å) of carbon dioxide measured under the same experimental conditions. The gas, stored in a 2-*l* flask with a pressure of about 50 mmHg at 293°K, was led into the apparatus through a nozzle 0.2 mm in diameter. The pressure in the apparatus was less than 1×10^{-4} mmHg during photographic exposure. The beam current was about 0.16 μA. Diffraction photographs were recorded on Fuji Process Hard plates.

Four photographs from each camera distance were traced with a microphotometer, and the optical densities were measured by an integrating digital voltmeter, TR-65A15.⁶⁾ Photographs were taken so as to keep the optical densities in the region proportional to the electron intensities.

Analysis

The electron intensity was analyzed by a standard least-squares method⁷⁾ after correction for small extraneous scattering. The calculations were made by using the HITAC 5020E at the Computation Center of the University of Tokyo. The experimental reduced molecular intensity, $qM(q)$, for q values of 16 to 120 was fitted to the theoretical expression by an estimated weight function:

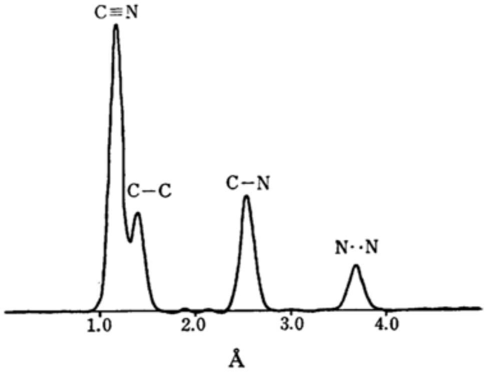

Fig. 2. Radial distribution curve for cyanogen.

$$qM(q) = k\sum c_{ij}\exp\left[-\frac{1}{2}l_{ij}^2\left(\frac{\pi}{10}\right)^2q^2\right]\times\sin\frac{\pi}{10}q\left[r_{aij}-\kappa_{ij}\left(\frac{\pi}{10}\right)^2q^2\right]\Big/r_{aij} \qquad (1)$$

The asymmetry parameters, κ, were fixed at their estimated values,⁸⁾ $\kappa(\mathrm{C{\equiv}N})=5.5\times10^{-7}$ Å³ and $\kappa(\mathrm{C{-}C})=12.0\times10^{-7}$ Å³. The κ parameters for nonbonded atom pairs were assumed to be zero. Figure 1 shows some typical reduced molecular intensities (experimental and best-fit) and the difference between the observed and the calculated values from the best-fit parameters. The r_a distances and the mean amplitudes obtained from the above analysis are listed in Table 1, along with their limits of error, which were estimated from

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6) Y. Morino, K. Kuchitsu and T. Fukuyama, This Bulletin, **40**, 423 (1967).

7) Y. Morino, K. Kuchitsu and Y. Murata, *Acta Cryst.*, **18**, 549 (1965).

8) K. Kuchitsu, This Bulletin, **40**, 498 (1967).

TABLE 1. INTERNUCLEAR DISTANCES, MEAN AMPLITUDES AND SHRINKAGES OF CYANOGEN (in Å units)

	r_a	l_{obs}	l_{calc}
C≡N	$1.162_3 \pm 0.001_9$	$0.035_3 \pm 0.000_8$	0.0347
C-C	$1.391_3 \pm 0.002_2$	$0.041_6 \pm 0.002_6$	0.0428
C·N	$2.542_3 \pm 0.003_5$	$0.050_8 \pm 0.001_3$	0.0470
N··N	$3.695_9 \pm 0.005_8$	$0.056_3 \pm 0.004_0$	0.0515

	r_g	δ_{obs}	δ_{calc}
C≡N	1.163_4	—	—
C-C	1.392_5	—	—
C·N	2.543_3	$0.012_6 \pm 0.004_5$	0.011
N··N	3.696_7	$0.022_6 \pm 0.006_8$	0.024

the internal consistency and the reproducibility of the results from four sets of electron intensities. The last column of Table 1 gives the values of the mean amplitudes calculated by the use of quadratic force constants. The F_{11}, F_{12}, and F_{22} force constants were calculated from the ν_1 and ν_2 for $^{12}C_2{}^{14}N_2$ and from the ν_1 for $^{12}C_2{}^{15}N_2$, which was estimated from the $\nu_1+\nu_5$ for this isotopic species by the use of the ν_5 and x_{55} for the normal species;4) they were found to be $F_{11}=16.78$, $F_{12}=0.42$, and $F_{22}=6.71$ md/Å. The other force constants were determined uniquely from the vibrational frequencies, since the secular equations are all one-dimensional: $F_{33}=17.73$, $F_{44}=0.18$, and $F_{55}=0.17$ md/Å. The observed shrinkage effects, δ_g, agree with the calculated values reported by Cyvin and Meisingseth,9) and are shown in Table 1.

Average Distances

With the force constants obtained above, the zero-point average distance, $r_\alpha{}^0$, was derived from r_a in three steps:5) (i) The thermal average of the instantaneous internuclear distance was calculated by:

$$r_g = r_a + l^2/r_a \tag{2}$$

(ii) The r_g distance was converted to the absolute-zero temperature:

$$r_g(0°\text{K}) = \lim(T \rightarrow 0°\text{K})r_g \tag{3}$$

(iii) The average distance, $r_\alpha{}^0$, was obtained by the subtraction of the centrifugal correction and the perpendicular contribution:

$$r_\alpha{}^0 = r_g(0°\text{K}) - (\langle \Delta x^2 \rangle_0 + \langle \Delta y^2 \rangle_0)/2r_e - \delta r \tag{4}$$

In the second step the parameters characterizing the anharmonicity of the bond-stretching vibrations were assumed to be equal to those of the corresponding diatomic molecules. The anharmonic term, $\langle \Delta z \rangle$, which is latent in the expression of r_g, was estimated for bonded atom pairs in a way described elsewhere.5) Those for nonbonded atom pairs were calculated by the summation of the linear terms for the constituent bonded pairs. The mean-square perpendicular and parallel amplitudes of vibration, $\langle \Delta x^2 \rangle$, $\langle \Delta y^2 \rangle$ and $\langle \Delta z^2 \rangle$ were calculated by the general formulas given by Morino and Hirota.10)

The $r_\alpha{}^0$ distances determined in this way, listed in Table 2, are essentially equivalent to the spectroscopic distances, r_z, between the average positions of the atoms in the ground vibrational state.

TABLE 2. ZERO-POINT AVERAGE DISTANCES FROM ELECTRON DIFFRACTION (in Å units)

	$r_\alpha{}^0$		$r_\alpha{}^0$
C≡N	$1.156_6 \pm 0.002_0$	C·N	$2.544_3 \pm 0.003_5$
C-C	$1.388_8 \pm 0.002_2$	N··N	$3.707_0 \pm 0.005_8$

TABLE 3. AVERAGE MOMENTS OF INERTIA FOR $^{12}C_2{}^{14}N_2$ AND $^{12}C_2{}^{15}N_2$ (in amu Å² units)

	$^{12}C_2{}^{14}N_2$	$^{12}C_2{}^{15}N_2$	
$I_\alpha{}^0$(ED)	107.53 ± 0.35	114.36 ± 0.38	
I_z(IR)	107.27 ± 0.03	114.09 ± 0.03	set A[a)]
	107.31 ± 0.03	114.12 ± 0.03	set B[a)]

a) See Ref. 4.

The average distances are shown to be additive:

$$r_\alpha{}^0(\text{C}\cdot\cdot\text{N}) - r_\alpha{}^0(\text{C-C}) - r_\alpha{}^0(\text{C}{\equiv}\text{N}) = -0.001_1 \pm 0.004_6\ \text{Å}$$

and:

$$r_\alpha{}^0(\text{N}\cdot\cdot\text{N}) - 2r_\alpha{}^0(\text{C}{\equiv}\text{N}) - r_\alpha{}^0(\text{C-C}) = 0.005_0 \pm 0.006_8\ \text{Å}$$

The linearity of the molecule has thus been confirmed by the present study of gas electron diffraction. The moments of inertia, $I_\alpha{}^0$, of $^{12}C_2{}^{14}N_2$ and $^{12}C_2{}^{15}N_2$ corresponding to the $r_\alpha{}^0$ distances are listed in Table 3.

Average Moment of Inertia as Detemined by Infrared Spectrocopy

The moment of inertia, I_z, for the average configuration was calculated from the effective rotational constant for the ground vibrational state, B_0, by11):

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9) S. J. Cyvin and E. Meisingseth, *Acta Chem. Scand.*, **15**, 1289 (1961).

10) Y. Morino and E. Hirota, *J. Chem. Phys.*, **23**, 737 (1955).

11) V. W. Laurie and D. R. Herschbach, *ibid.*, **37**, 1687 (1962).

$$I_z=\frac{h}{8\pi^2B_0}-\frac{h}{8\pi^2}\times\left[\frac{1}{\omega_1}+\frac{1}{\omega_2}+\frac{1}{\omega_3}+\frac{1}{\omega_4}+\frac{1}{\omega_5}-\frac{4}{\omega_3+\omega_5}-4(\zeta_{14})^2\left(\frac{1}{\omega_2}+\frac{1}{\omega_1+\omega_4}\right)-4(\zeta_{24})^2\left(\frac{1}{\omega_1}+\frac{1}{\omega_2+\omega_4}\right)\right]\qquad(5)$$

The correction term was calculated to be -0.012 amu Å^2. The average moments of inertia are listed in Table 3.

Average Structure of Cyanogen

The average moments of inertia obtained from electron diffraction and from infrared spectroscopy agree well with each other, differing only about 0.24%. The difference is within the limit of error of the electron-diffraction experiment. Infrared spectroscopy gives moments of inertia more accurate than those of electron diffraction. On the other hand, uncertainties in the spectroscopic bond distances are still a few hundredths of an angstrom, as assigned by Maki.⁴⁾ The principal reasons for this are that the distances derived from the isotopic moments of inertia are sensitive to small errors in the moments (as is illustrated in Fig. 3) and that the dependence of the average bond distances on isotopic substitution is uncertain. On the other hand, the essential part of the above-mentioned discrepancy in the moments of inertia can be ascribed to the systematic error of 0.12% in the measurement of the electron wavelength. Such being the circumstances, the scale factor was calibrated by the spectroscopic moments of inertia (Maki's set A); the corrected average bond distances turned out to be:

$$r_z(\text{C}\equiv\text{N})=1.155_2\pm0.001_3\ \text{Å}$$

and:

$$r_z(\text{C–C})=1.387_1\pm0.001_4\ \text{Å}$$

The use of his alternative set, B, which was regarded by Maki as less plausible, led to an increase of 0.0002 Å in both distances. The r_z structure obtained above is, accidentally, close to the effective r_0 structure reported by Maki.

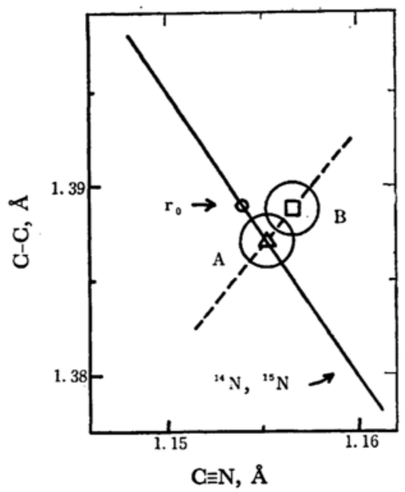

Fig. 3. Plot of the C–C distance *versus* the C–N distance in cyanogen. The solid line represents the relationship between the distances r(C–C) and r(C≡N). Two lines for $^{12}C_2{}^{14}N_2$ and $^{12}C_2{}^{15}N_2$ are virtually indistinguishable in the region shown in the figure. The broken line is a locus of the most probable distances as the electron-diffraction scale factor is varied. The square corresponds to the $r_\alpha{}^0$ distances observed by electron diffraction, while the triangle represents the average distances r_z. The circles indicate the limits of random error in electron-diffraction experiment. The limits of uncertainties of the r_z parameters are set by the crossings of the solid lines and the circle A. The limits of error of the r_0 distances reported by Maki (±0.030 Å for C–C and ±0.017 Å for C–N) are outside the illustrated region.

The CC bond length determined above is about 0.01 Å longer than the value expected from the empirical rule proposed by Stoicheff,[12] $r(\equiv\text{C–C}\equiv)=1.299+0.040\times2=1.379$ Å. This slight discrepancy can be explained, at least qualitatively, in terms of the difference in bond order. The details will be published in a forthcoming paper.

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12) B. P. Stoicheff, *Tetrahedron*, **17**, 135 (1962).