February, 1974] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(2), 299—304 (1974) 299

# Molecular Structures of Hydrogen Cyanide and Acetonitrile as Studied by Gas Electron Diffraction

Ken-ichi Karakida, Tsutomu Fukuyama, and Kozo Kuchitsu
*Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113*

(Received October 27, 1973)

The structures of HCN and $CH_3CN$ have been determined by gas electron diffraction for a critical comparison between diffraction and spectroscopic data. For HCN, the $r_g$(C≡N), determined by gas electron diffraction, $1.158 \pm 0.003$ Å, is consistent within the estimated limit of experimental error with that calculated from the spectroscopic $r_e$ structure and the harmonic and anharmonic force constants by a perturbation procedure, $1.158_8$ Å. For $CH_3CN$, electron diffraction intensities have been analyzed jointly with the rotational constants for the normal and three deuterated species determined by microwave spectroscopy by Kessler *et al.* and Thomas *et al.* The isotopic difference in the average C–H distance, $\delta r = r_{av}(\text{C–H}) - r_{av}(\text{C–D})$, has also been treated as one of the independent parameters. The analysis has led to the following structure: $r_g$(C≡N) = $1.159 \pm 0.002$ Å, $r_g$(C–C) = $1.468 \pm 0.002$ Å, $r_g$(C–H) = $1.107 \pm 0.004$ Å, ∠C–C–H ($r_{av}$) = $109.7 \pm 0.2°$ and $\delta r = 0.001 \pm 0.002$ Å.

The purpose of the present determination of the $r_g$ structures of hydrogen cyanide and acetonitrile is twofold. First, a comparison of the structures is made with those of analogous molecules with conjugated multiple bonds in pursuit of a systematic variation in the C–C and C≡N bond lengths with environment.[1,2] Second, a comparison is made of the structures determined by electron diffraction (ED) with those determined by spectroscopic (SP) methods, since these molecules are suitable examples for a critical check of SP and ED structures.

For HCN the equilibrium ($r_e$) structure[3] and the potential constants (up to the quartic)[4] have been determined by infrared spectroscopy with such precision that the $r_g$ structure can be calculated purely from spectroscopic data by a perturbation procedure.[5] A comparison of ED and SP structures should then afford a direct test of the experimental accuracy and the theory of ED[5–7] on which our method is founded. Our attention has primarily been called to the C≡N distance, since the accuracy of the C–H distance determined by ED is not sufficient for such a critical comparison. Similar studies have already been made for a number of molecules, for which $r_e$ structures and potential constants are well known by spectroscopy (diatomics, $CO_2$, $CS_2$, $NH_3$, $CH_4$, *etc.*), and in all cases the structures are reported to be fully consistent.[2] However, there still remain unsolved problems important for the application of the method to more complicated systems. For instance, for diacetylene[8] the bond lengths, mean amplitudes and rotational constants derived from ED appeared to be slightly different from those determined by SP, and the small discrepancies were tentatively ascribed to a cubic potential term representing bending-stretching interactions.

Furthermore, the hydrogen-deuterium isotope effect on the average structure is another important problem, which has by no means been settled, for a combined analysis of ED and SP measurements. Acetonitrile was selected in this study because of its simplicity, high symmetry, well-defined quadratic force field, and the absence of low frequency motions such as internal rotation.

The ED structure of $CH_3CN$ was reported to be[9] $r$(C–C) = $1.54 \pm 0.02$ Å and $r$(C≡N) = $1.16 \pm 0.02$ Å, or[10] $r$(C–C) = $1.49 \pm 0.03$ Å and $r$(C≡N) = $1.16 \pm 0.03$ Å, where the C–H distance and CCH angle were assumed. The $r_0$ structure was determined from ten rotational constants for eight isotopic species determined by microwave spectroscopy.[11–14] Besides the C–H, C≡N, C–C distances and CCH angle, $r_0$(C–D) and the CCD angle were taken as independent parameters.[14] The isotope effects on the $r_0$ structure were: $r_0$(C–H) − $r_0$(C–D) = 0.0048 Å and ∠CCH − ∠CCD = 0.1°. The isotopic rotational constants were used by Costain[15] and Matsumura *et al.*[16] to determine the $r_s$ structure by Kraitchman's equations. The $r_s$ and $r_0$ structures are compared with the $r_g$ structure determined in the present analysis in a later section.

## Experimental

A sample of hydrogen cyanide (bp 26 °C) was prepared by adding sulfuric acid to sodium cyanide. The vessel was filled with dry nitrogen and the product was trapped in ice-cold water. The crude product containing water was purified by passing it through a tube heated to about 40 °C packed with calcium chloride. Acetonitrile was obtained from a commercial source (purity 96%, bp 81 °C) and used after distillation. The infrared spectra of HCN gas and $CH_3CN$ liquid showed no band that could be assgined to impurities.

Electron diffraction photographs were taken with an apparatus equipped with an $r^3$-sector[17] at camera lengths of 107.8 and 243.2 mm. The electron wavelength was about 0.06 Å. The sample gases were maintained in thermal equilibrium with their liquid phase at 0 °C for HCN and at room temperature for $CH_3CN$. The pressures of the samples were about 250 and 70 Torr for HCN and $CH_3CN$, respectively. The exposure time for the shorter camera length was about 40 s for each sample, while that for the longer camera length was about one-third of that. Other experimental details are described elsewhere.[17,18]

The scale factor was calibrated with reference to the $r_a$(C=O) distance ($1.164_6$ Å) of carbon dioxide measured with the identical camera geometry. The accelerating voltage was monitored during photographic exposures. The observed $r_a$(C=O) distance and its standard deviation were $1.1649 \pm 0.0004$ Å. Besides this calibration, the $r_a$(N≡N) of nitrogen (theoretical, $1.100_7$ Å[19]) was also measured, and it was confirmed that carbon dioxide and nitrogen gave consistent scale factors.

Observed molecular intensities covering the range $s = 3.5$–$37.7$ Å$^{-1}$ were used in the analysis. The data taken with

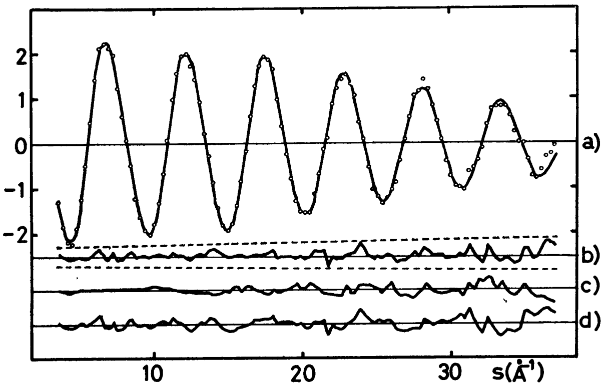

Fig. 1. a) Experimental and best-fit molecular intensities for HCN shown in dots and solid curves, respectively.

b) Experimental minus best-fit theoretical. The broken curve represents the estimated limit of random error in the molecular intensity (corresponding to a relative error of $1\times10^{-3}$ in the original photocurrent).

c) Typical difference between two molecular intensity data used in the analysis illustrating the degree of reproducibility.

d) The observed minus theoretical molecular intensity calculated from spectroscopic parameters.

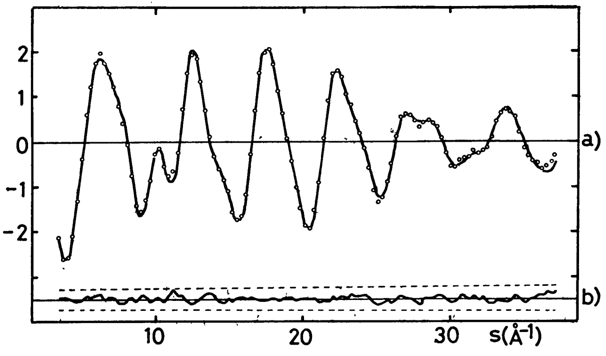

Fig. 2. a) Experimental and best-fit molecular intensities for $CH_3CN$ shown in dots and solid curves, respectively.

b) See caption b) of Fig. 1.

the short and long camera lengths were linked at $s=13.8$ and 11.9 Å$^{-1}$ for HCN and $CH_3CN$, respectively.[20] The elastic and inelastic scattering factors and the phase shifts were taken from the tables prepared by Bonham *et al.*[21] The molecular intensities are illustrated in Figs. 1 and 2 for HCN and $CH_3CN$, respectively, and the corresponding radial distribution curves are given in Figs. 3 and 4. For a representation of the reproducibility of the molecular intensity data, a difference between two intensities for HCN selected arbitrarily is shown in Fig. 1 (c). The level of random scatter is similar to that of the residuals (observed minus calculated intensities) derived from a least-squares analysis.

## Analysis and Discussion

*HCN.* A linear equilibrium structure was assumed. A least-squares analysis was carried out with an empirical diagonal weight matrix.[22] The asymmetry parameters $\kappa$[19] for the C–H and C≡N bonds

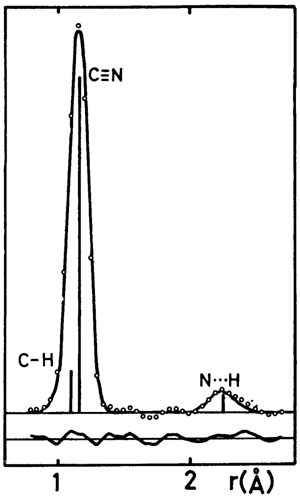

Fig. 3. Experimental (dots) and theoretical radial distribution curves for HCN. The lower curve represents residuals. Vertical bars correspond to internuclear distances. A damping factor, $\exp(-0.0016s^2)$, was used.

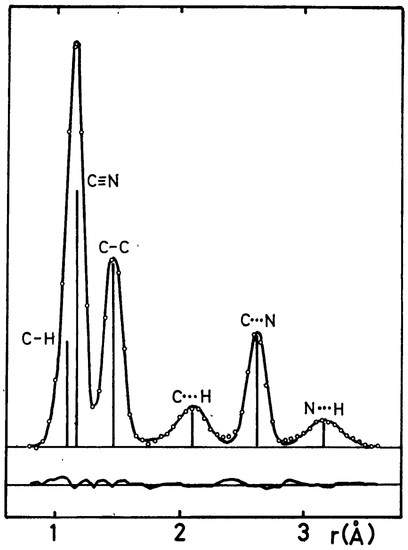

Fig. 4. Experimental and theoretical radial distribution curves for $CH_3CN$. See captions of Fig. 3.

TABLE 1. MOLECULAR PARAMETERS FOR HCN[a)] (in Å units)

| | C≡N | C-H | N---H |
|---|---|---|---|
| $r_g$(ED)[b)] | 1.158±0.003 | 1.10±0.02 | 2.24±0.02 |
| $r_g$(SP)[c)] | $1.158_8$ | $1.083_6$ | $2.226_0$ |
| $l_{obsd}$[b)] | 0.039±0.003 | 0.07±0.03 | 0.08±0.02 |
| $l_{calcd}$[c)] | $0.034_6$ | $0.075_8$ | $0.079_1$ |
| $\delta$[d)] | 0.0002 | 0.0174 | 0.0047 |

a) Uncertainties are estimated limits of error. b) Mean amplitudes, $l_m$ defined in Ref. 19, derived from the present analysis of electron diffraction intensities. They are estimated to be equal to $l_e$ within the quoted experimental error. c) Calculated values, $l_e$, based on spectroscopic $r_e$ distances, harmonic and anharmonic force constants. d) Shrinkage corrections, $r_a-r_\alpha$.

TABLE 2. ERROR MATRIX FOR $HCN^{a)}$

| | $k_1^{b)}$ | $k_2^{c)}$ | $l$(C-H) | $l$(N--H) | $l$(C≡N) | $r$(C-H) | $r$(C≡N) |
|---|---|---|---|---|---|---|---|
| $k_1$ | 134 | | | | | | |
| $k_2$ | 171 | 332 | | | | | |
| $l$(C-H) | 125 | 199 | 165 | | | | |
| $l$(N--H) | 35 | 42 | 31 | 97 | | | |
| $l$(C≡N) | 34 | 65 | 41 | 8 | 14 | | |
| $r$(C-H) | −13 | −63 | 52 | −13 | 11 | 74 | |
| $r$(C≡N) | −35 | −54 | −48 | −9 | −12 | −21 | 15 |

a) Units ($\times 10^{-4}$) for the distances are Å, those for the indices are dimensionless. b) Index of resolution for the long-camera region, $0.87\pm0.03$. c) Index of resolution for the short-camera region, $0.98\pm0.05$.

were estimated to be $1.7\times10^{-5}$ and $0.5\times10^{-6}$ Å$^3$ from the anharmonicity parameter $a_3$ for the diatomic molecules CH and CN,[23] 1.98 and 2.27 Å$^{-1}$, respectively. The $\kappa$ parameter for the nonbonded N–H pair was ignored. The vibrational corrections for the shrinkage effect[24] and the mean amplitudes of vibration ($d=r_a-r_\alpha$ and $l_{\text{calcd}}$, listed in Table 1) were calculated from the force constants.[4] The most probable $r_g$ distances and mean amplitudes are shown in Table 1 with their limits of error estimated from random and systematic uncertainties.[25] The error in the $r_g$(C≡N) distance originates mainly from the standard deviation in the least-squares analysis (0.0015 Å), and the uncertainties in the scale factor and in the shrinkage corrections (about 0.0006 Å and 0.0003 Å, respectively) are relatively unimportant. A slight discrepancy between the observed and calculated $l$(C≡N) may be ascribed to a systematic error in the observed mean amplitude due to extraneous scattering observed in large scattering angles. However, the $r_g$(C≡N) distance is not influenced significantly by this extraneous scattering. A typical error matrix is given in Table 2.

In order to compare the $r_g$ structure with the $r_e$ structure determined by infrared spectroscopy, the values of $r_g-r_e=\langle\Delta r\rangle$ were calculated by use of the anharmonic force constants[4] and perturbation theory.[5,26,27] Mean values of the internal coordinates are calculated from those of the normal coordinates (Table 3). Then thermal averages were taken with the Boltzmann factors, and corrections for centrifugal distortion[28] were included. In the present case, however, the normal frequencies are so high that the temperature corrections are negligible. The results are compared in Table 4 with those estimated by a diatomic approximation,[6,23] $\langle\Delta r\rangle=(3/2)a_3\langle\Delta r^2\rangle$. The $\langle\Delta r\rangle$ values calculated by perturbation theory are estimated to be accurate to about 0.0001 Å, and hence, the diatomic approximation is valid to the order of 0.002 Å (see Table 4). The $r_g$ structure calculated from the spectroscopic equilibrium structure are compared in Table 1 with those determined by electron diffraction. They are consistent with each other within the experimental error of the latter. This situation is illustrated in Fig. 1 (d) as a difference curve between the observed molecular intensity and that calculated from the spectroscopic parameters. The fluctuations of the difference curve are random and similar in magnitude to those of the least-squares residuals.

TABLE 3. MEAN VALUES OF THE NORMAL COORDINATES FOR $HCN^{a)}$

| | | | |
|---|---|---|---|
| $\langle Q\ \rangle$ | 0.00988 | $\langle Q_1Q_2^2\rangle$ | 0.00032 |
| $\langle Q\ \rangle$ | −0.00638 | $\langle Q_3Q_2^2\rangle$ | −0.00088 |
| $\langle Q_1^2\rangle$ | 0.00801 | $\langle Q_1^2Q_2^2\rangle$ | 0.00039 |
| $\langle Q_2^2\rangle$ | 0.04851 | $\langle Q_3^2Q_2^2\rangle$ | 0.00025 |
| $\langle Q_3^2\rangle$ | 0.00525 | $\langle Q_2^4\rangle$ | 0.00471 |

a) The normal coordinates are in (amu)$^{1/2}$Å.

TABLE 4. MEAN DISPLACEMENTS FOR $HCN^{a)}$ (at 300 K)

| | C N | C-H | N--H |
|---|---|---|---|
| $\langle\Delta r\rangle_{\text{calcd}}^{b)}$ | 0.0057 | 0.0177 | 0.0070 |
| $\langle\Delta r\rangle_{\text{approx}}^{c)}$ | 0.0040 | 0.0170 | — |

a) $\langle\Delta r\rangle$: in Å units. b) Calculated by perturbation theory. c) Calculated by a diatomic approximation, $\langle\Delta r\rangle=(3/2)a_3\langle\Delta r^2\rangle$, with $a_3$ assumed to be 1.98 Å$^{-1}$ and 2.27 Å$^{-1}$ for C-H and C≡N, respectively.

*$CH_3CN$.* The equilibrium structure was assumed to have $C_{3v}$ symmetry. The $\kappa$ parameters were estimated to be $1.9\times10^{-5}$, $2.0\times10^{-6}$ and $0.5\times10^{-6}$ Å$^3$ for C–H, C–C and C≡N, respectively.[19]

The most probable $r_\alpha^0$ distances and angle obtained from a least-squares analysis are shown in Table 5 with estimated uncertainties.[25] The most probable

TABLE 5. AVERAGE STRUCTURES OF $CH_3CN^{a)}$ (in Å units)

| | $r_\alpha^{0\ b)}$ | $r_{\text{av}}^{c)}$ | $r_z^{d)}$ |
|---|---|---|---|
| C-C | $1.464\pm0.002$ | $1.465\pm0.002$ | $1.45_9\pm0.01_5$ |
| C N | $1.154\pm0.002$ | $1.153\pm0.002$ | $1.15_9\pm0.01_5$ |
| C-H | $1.102\pm0.015$ | $1.095\pm0.004$ | $1.10_0\pm0.02$ |
| ∠CCH | $110.1\pm0.8°$ | $109.7\pm0.2°$ | $109.7\pm0.4°$ |
| $\delta r^{e)}$ | — | $0.001\pm0.002$ | $(0.002\pm0.005)$ |

a) Uncertainties are estimated limits of error. b) Derived from electron diffraction data. c) Derived from electron diffraction intensities plus rotational constants for the normal species and three deuterated species. d) Derived from twelve rotational constants. The difference, $\delta r$, in the $r_z$(C-H) distance with isotopic substitution (H to D) was assumed to be $0.002\pm0.005$Å and those in the $r_z$(C-H), $r_z$(C-C) and $r_z$(C≡N) distances with isotopic substitutions ($^{12}C$ to $^{13}C$ and $^{14}N$ to $^{15}N$) were assumed to be $0\pm0.0003$Å. The secondary isotopic differences in the C-C and C≡N distances in $CH_3CN$ and $CD_3CN$ were ignored. e) Isotopic difference in the C-H bond length, $r$(C-H)-$r$(C-D).

TABLE 6. OBSERVED AND CALCULATED MEAN AMPLITUDES AND SHRINKAGE CORRECTIONS FOR $CH_3CN$ (in Å units)

| | $l_{obsd}$[a)] | $l_{calcd}$[b)] | $r_a - r_\alpha$[c)] |
|---|---|---|---|
| C-C | 0.048±0.003 | 0.0483 | 0.0023 |
| C≡N | 0.036±0.003 | 0.0342 | 0.0060 |
| C-H | 0.075±0.009 | 0.0780 | 0.0071 |
| C---N | 0.055±0.005 | 0.0505 | −0.0007 |
| C---H | 0.102[d)] | 0.1020 | 0.0036 |
| N---H | 0.120[d)] | 0.1196 | −0.0021 |
| H---H | 0.126[d)] | 0.1260 | 0.0032 |

a) See footnotes a) and b) of Table 1. b) Parallel mean square amplitudes, $\langle \Delta z^2 \rangle^{1/2}$, calculated from Urey-Bradley force constants. c) Calculated shrinkage corrections. d) Fixed at calculated values.

mean amplitudes are listed in Table 6, where the corresponding theoretical values and the shrinkage corrections,[24)] $d = r_a - r_\alpha$, calculated from Urey-Bradley force constants[29)] are also given. The mean amplitudes of nonbonded pairs including hydrogen were fixed at the calculated values and the rest of the parameters were varied in the analysis.

The $r_\alpha$ parameters determined by the ED analysis were extrapolated to zero kelvin using a diatomic approximation for the bonded parameters[24)] and neglecting temperature dependence of the angle parameter. The rotational constant calculated from the $r_\alpha{}^0$ parameters, $B_\alpha{}^0(\mathrm{ED}) = 0.3063 \pm 0.0015\ \mathrm{cm}^{-1}$, was consistent with its spectroscopic counterpart $B_z(\mathrm{Mw}) = 0.30661_7 \pm 0.00002\ \mathrm{cm}^{-1}$. Therefore, the diffraction and spectroscopic data were combined.

The rotational constants $B_0$ have been reported for the normal and seven other symmetric-top species, and $B_0$ and $C_0$ for two asymmetric species.[11–14,16)] The rotational constants for all the isotopic species were not used for determining the average structure, however, because small uncertainties in the isotopic differences in the structure can influence the result of the analysis.[30–32)] The uncertainties in the $r_z$ structures shown in Table 5 originate mainly from those in the isotopic differences. Accordingly, the rotational constants for the normal species and three deuterated species ($CD_3CN$, $CD_2HCN$ and $CDH_2CN$) were selected as additional data after transforming them into the average rotational constants, $B_z$ and $C_z$.[28)] Instead of assuming the isotopic difference $\delta r = r_{av}(\mathrm{C{-}H}) - r_{av}(\mathrm{C{-}D})$, it was taken as an independent parameter in the present least-squares analysis. This procedure avoids a systematic error originating from an assumed $\delta r$ value. The isotopic difference for ∠CCH−∠CCD was assumed to be 0±0.1°, and those for the other parameters were ignored. The weights for the rotational constants in the analysis were adjusted to $1 \times 10^7$ for $B_z$ and $C_z$ in comparison with a unit weight assigned to the molecular intensities from $s = 6.3$ to $26.7\ \text{Å}^{-1}$ taken at $\pi/10$ intervals. The error matrix is given in Table 7.

The average structure, $r_{av}$, thus determined is compared in Table 5 with the $r_\alpha{}^0$ structure determined in the foregoing ED analysis. The $r_{av}$ structure is not significantly different from the $r_\alpha{}^0$ structure determined from the diffraction data alone except that the hydrogen parameters are appreciably more accurate. The $\delta r$ value is probably only slightly positive, in contrast to that calculated from the conventional method given in Ref. 32 as Eq. (2), $0.002_6$ Å. The rotational constants are compared in Table 8.

The $r_z$ structure determined from twelve rotational constants is also shown in Table 5, where the quoted uncertainties result mainly from those in the isotopic differences in the $r_z$ distances, though the differences themselves are estimated to be very small. The change $\delta r$ in the C–H distance upon substitution of H by D was assumed to be 0.002±0.005 Å and the changes in the C–H, C–C and C≡N distances upon substitutions of the $^{12}$C nucleus by $^{13}$C and $^{14}$N by $^{15}$N were assumed to be 0±0.0003 Å. The effect of the isotopic difference in the angle, ∠CCH−∠CCD, was assumed to be 0±0.1°. The secondary isotopic differences[33,34)] in the C–C and C≡N distances in $CH_3CN$ and $CD_3CN$ were ignored.

Table 5 shows that the ED and SP data supply complementary information on the determination of precise skeletal and hydrogen structures, respectively. The C–C and C≡N distances are determined uniquely from ED intensities without recourse to the rotational constants for the $^{13}$C and $^{15}$N species. It is also possible

TABLE 7. ERROR MATRIX FOR $CH_3CN$[a)]

| | $k_1$[b)] | $k_2$[c)] | $l$(C-C) | $l$(C≡N) | $l$(C-H) | $l$(C--N) | $r$(C-C) | $r$(C≡N) | $r$(C-H) | ∠CCH | $\delta r$[d)] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $k_1$ | 191 | | | | | | | | | | |
| $k_2$ | 192 | 303 | | | | | | | | | |
| $l$(C-C) | 40 | 66 | 17 | | | | | | | | |
| $l$(C≡N) | 40 | 62 | 14 | 14 | | | | | | | |
| $l$(C-H) | 76 | 93 | 19 | 19 | 45 | | | | | | |
| $l$(C--N) | 39 | 59 | 13 | 12 | 19 | 18 | | | | | |
| $r$(C-C) | 18 | 21 | 3 | 4 | 14 | 4 | 7 | | | | |
| $r$(C≡N) | −20 | −23 | −4 | −5 | −15 | −5 | −6 | 7 | | | |
| $r$(C-H) | −22 | −31 | −7 | −5 | −8 | −6 | 2 | −3 | 17 | | |
| ∠CCH | 22 | 27 | 6 | 4 | 7 | 5 | −6 | 3 | −12 | 14 | |
| $\delta r$ | 9 | 7 | 1 | 2 | 5 | 2 | −2 | −2 | 9 | 5 | 11 |

a), b), c) See corresponding footnotes of Table 2. The indices of resolution are 0.97±0.03 and 0.94±0.03 for $k_1$ and $k_2$, respectively. Units for the angle is $10^{-4}$ radian. d) $r$(C-H)−$r$(C-D).

TABLE 8. ROTATIONAL CONSTANTS FOR $CH_3CN$[a] (in $cm^{-1}$)

| | | 0[b] | z[c] | av[d] |
|---|---|---|---|---|
| $CH_3CN$ | $B$ | 0.306840 | 0.30662 (2) | 0.30664 (5) |
| $CH_2DCN$ | $B$ | 0.292175 (2) | 0.29190 (2) | 0.29192 (3) |
| | $C$ | 0.287149 (2) | 0.28699 (2) | 0.28698 (5) |
| $CHD_2CN$ | $B$ | 0.277527 (2) | 0.27727 (2) | 0.27728 (3) |
| | $C$ | 0.272336 (2) | 0.27218 (2) | 0.27216 (4) |
| $CD_3CN$ | $B$ | 0.262112 | 0.26192 (2) | 0.26190 (3) |

a) Uncertainties attached to the last significant digits are given in parentheses. b) Observed rotational constants ($B_0$ and $C_0$) taken from Refs. 11 and 14. Uncertainties for $CH_3CN$ and $CD_3CN$ were not given. c) Average rotational constants calculated from $B_0$ and $C_0$ with corrections for vibrational effects. The limits of error are estimated from the uncertainties in the quadratic force constants used for calculating the corrections. d) Best-fit rotational constants corresponding to the $r_{av}$ structure listed in Table 5, derived from a combined analysis of electron-diffraction and microwave data. Uncertainties represent 2.5 times the estimated standard deviations.

TABLE 9. COMPARISON OF $r_g$, $r_s$ AND $r_0$ STRUCTURES FOR $CH_3CN$ (in Å units)

| | $r_g$[a] | $r_s$[b] | $r_0$[c] |
|---|---|---|---|
| C-C | 1.468±0.002 | 1.4584 | 1.4582 |
| C N | 1.159±0.002 | 1.1571 | 1.1572 |
| C-H | 1.107±0.004 | 1.1036 | 1.1120 |
| ∠CCH | 109.7±0.2° [d] | 109.45° | 109.67° |
| $r$(CH)-$r$(CD) | 0.001±0.002[e] | 0.0022 | 0.0048 |
| ∠CCH-∠CCD | (0±0.1°)[e,f] | 0.10° | 0.08° |

a) Derived from the $r_{av}$ structure determined in the present study. b) Refs. 15, 16. No estimates of uncertainties are given. c) Ref. 14. No estimates of uncertainties are given. d) $r_{av}$ structure. e) Isotopic differences based on the $r_{av}$ structure. f) Assumed value.

to vary $\delta r$ as one of the parameters. Hence, a major part of the uncertainties resulting from the assumptions about unknown isotopic differences are eliminated, and the precision of these parameters is thereby improved by nearly an order of magnitude.

The $r_g$ structure derived from the $r_{av}$ structure determined in the present study is compared with the $r_s$[15,16] and $r_0$ structures[14] in Table 9.* Particularly significant is the discrepancy of about 0.01 Å observed in the $r_g$(C–C) and $r_s(r_0)$(C–C) distances. The $r_g$(C≡N) and $r_g$(C–C) bond distances in acrylonitrile,[35] cyanogen,[36] acetonitrile and hydrogen cyanide are compared in Table 10. The $r_g$(C≡N) in acrylonitrile is longer than those in the other molecules. The $r_g$(C–C) in acetonitrile is significantly longer than those in acrylonitrile and cyanogen.

TABLE 10. COMPARISON OF C≡N AND C-C DISTANCES IN ANALOGOUS MOLECULES (in Å units)

| | $r_g$(C≡N) | $r_g$(C-C) |
|---|---|---|
| $CH_2$=CH-C≡N[a] | 1.167±0.004 | 1.438±0.003 |
| N≡C-C≡N[b] | 1.163±0.002 | 1.393±0.002 |
| $H_3$C-C≡N[c] | 1.159±0.002 | 1.468±0.002 |
| H-C≡N[c] | 1.158±0.003 | — |

a) Ref. 35. b) Ref. 36. c) Present study.

The authors wish to thank Professor Robert K. Bohn for his helpful comments on the manuscript and Mr. Masaaki Sugié, Mr. Ichiro Minami and Mr. Takeo Kishimoto for their technical help in the experiment and analysis.

## References

1) Y. Morino, K. Kuchitsu, T. Fukuyama, and M. Tanimoto, *Acta Crystallogr.*, **A 25**, S 127 (1969).

2) K. Kuchitsu, "Gas Electron Diffraction," MTP International Review of Science, A Biennial Series, Physical Chemistry, Vol. 2, Chapter 6, G. Allen, Ed., Medical and Technical Publishing, Co., Oxford (1972).

3) D. H. Rank, G. Skorinko, D. P. Eastman, and T. A. Wiggins, *J. Opt. Soc. Amer.*, **50**, 421 (1960).

4) T. Nakagawa and Y. Morino, This Bulletin, **42**, 2212 (1969).

5) K. Kuchitsu and L. S. Bartell, *J. Chem. Phys.*, **36**, 2460 (1962).

6) L. S. Bartell, *ibid.*, **23**, 1219 (1955).

7) Y. Morino, K. Kuchitsu, and T. Oka, *ibid.*, **36**, 1108 (1962).

8) M. Tanimoto, K. Kuchitsu, and Y. Morino, This Bulletin, **44**, 386 (1971).

9) L. O. Brockway, *J. Amer. Chem. Soc.*, **58**, 2516 (1936).

10) L. Pauling, H. D. Springall, and K. J. Palmer, *ibid.*, **61**, 927 (1939).

11) M. Kessler, H. Ring, R. Trambarulo, and W. Gordy, *Phys. Rev.*, **79**, 54 (1950).

12) D. K. Coles, W. E. Good, and R. H. Hughes, *ibid.*, **79**, 224 (1950).

13) R. Trambarulo and W. Gordy, *ibid.*, **79**, 224 (1950).

14) L. F. Thomas, E. I. Sherrad, and J. Sheridan, *Trans. Faraday Soc.*, **51**, 619 (1955).

15) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).

16) C. Matsumura, E. Hirota, T. Oka, and Y. Morino, *J. Mol. Spectrosc.*, **9**, 366 (1962).

17) Y. Murata, K. Kuchitsu, and M. Kimura, *Jap. J. Appl. Phys.*, **9**, 591 (1970).

18) M. Tanimoto, K. Kuchitsu, and Y. Morino, This Bulletin, **43**, 2776 (1970).

19) K. Kuchitsu, *ibid.*, **40**, 498 (1967).

20) Numerical experimental data of the leveled total intensity have been deposited with the Chemical Society of Japan (Document No. 7405).

21) L. Schäfer, A. C. Yates, and R. A. Bonham, *J. Chem. Phys.*, **55**, 3055 (1971).

22) Y. Morino, K. Kuchitsu, and Y. Murata, *Acta Crystallogr.*, **18**, 549 (1965).

23) K. Kuchitsu and Y. Morino, This Bulletin, **38**, 805 (1965).

24) K. Kuchitsu and S. J. Cyvin, "Molecular Structures and Vibrations," ed. by S. J. Cyvin, Chapter 12, Elsevier, Amsterdam (1972).

---

* **Note added in proof**: A more precise $r_0$ structure of acetonitrile has recently been determined: J. L. Duncan, D. C. McKean, and N. D. Michie, *J. Mol. Structure,* **23** (1974), in press.

25) K. Kuchitsu, "Molecular Structures and Vibrations," ed. by S. J. Cyvin, Chapter 10, Elsevier, Amsterdam (1972).

26) Y. Morino and T. Iijima, This Bulletin, **35**, 1661 (1962).

27) K. Kuchitsu, *ibid.*, **40**, 505 (1967).

28) M. Toyama, T. Oka, and Y. Morino, *J. Mol. Spectrosc.*, **13**, 193 (1964).

29) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **18**, 513 (1962).

30) V. W. Laurie and D. R. Herschbach, *J. Chem. Phys.*, **37**, 1687 (1962).

31) W. J. Lafferty, D. R. Lide, and R. A. Toth, *ibid.*, **43**, 2063 (1965).

32) K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Structure*, **4**, 41 (1969).

33) L. S. Bartell and H. K. Higginbotham, *J. Chem. Phys.*, **42**, 851 (1965).

34) R. H. Schwendeman and J. D. Kelly, *ibid.*, **42**, 1132 (1965).

35) T. Fukuyama and K. Kuchitsu, *J. Mol. Structure*, **5**, 131 (1970).

36) Y. Morino, K. Kuchitsu, Y. Hori, and M. Tanimoto, This Bulletin, **41**, 2349 (1968).