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# Molecular Structure of Diacetylene as Studied by Gas Electron Diffraction

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The molecular structure of diacetylene has been studied by gas electron diffraction. Thermal-average bond distances are determined to be: $r_g$(C–C)$=1.383_7\pm0.001_9$ Å, $r_g$(C≡C)$=1.217_6\pm0.001_4$ Å, and $r_g$(C–H)$=1.093_5\pm0.010$ Å. The C–C single bond is about 0.007 Å shorter than that in cyanogen, while the C≡C triple bond is about 0.005 Å longer than that in acetylene. The observed mean amplitudes are slightly larger than the parallel amplitudes based on harmonic calculations. A suggestion has been made to account for the discrepancies by the use of empirical constants representing the interaction between bending and bond-stretching vibrations, which makes the bond distances slightly longer, on the average, in a momentary bent structure than in a linear structure. This interaction also seems to account for a slight difference between the rotational constant $B_0$ estimated from the above $r_g$ distances and those derived from spectroscopic experiments.

At an early stage of the structure studies by modern methods, Herzberg *et al.*[1] and Pauling *et al.*[2] remarked that a C–C single bond adjacent to a triple bond was shorter than that in saturated hydrocarbons. Subsequently, systematic analyses of experimental data led Stoicheff *et al.*[3] to an empirical rule that a C–C bond distance increases linearly with the number of adjacent atoms. According to Stoicheff,[4] this rule was applicable to most of the C–C distances reported up to 1962 within the uncertainty of 0.005 Å.

There are, however, a number of basic molecules which require further experimental studies. By the use of the recent technique of gas electron diffraction, the structure of some of the molecules studied previously can be determined with somewhat higher accuracy. Thus, from the studies of a number of conjugated aliphatic hydrocarbons with or without heteroatoms, a significant heteroatom effect on the C–C bond distance has been observed.[5–7] As for the molecules with a C–C bond between two triple bonds (the *sp-sp* system), the structure of cyanogen (N≡C–C≡N) was determined by electron diffraction[8] in combination with the rotational constant obtained from high-resolution infrared spectroscopy.[9] The $r_g$, C–C bond distance, was found to be about 0.01 Å larger than the value expected from the Stoicheff rule.

On the other hand, none of the previous studies of the diacetylene (HC C–C≡CH) structure by means of electron diffraction,[2] infrared,[10,11] and rotational

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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. Amer. Chem. Soc.*, **61**, 927 (1939).

3) G. Herzberg and B. P. Stoicheff, *Nature*, **175**, 79 (1955); C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.*, **30**, 777 (1959).

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

5) K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Structure*, **1**, 463 (1968).

6) K. Kuchitsu, T. Fukuyama, and Y. Morino, *ibid.*, **4**, 41 (1969).

7) T. Fukuyama and K. Kuchitsu, *ibid.*, **5**, 131 (1970).

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

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

10) A. V. Jones, *ibid.*, **20**, 860 (1952).

11) G. D. Craine and H. W. Thompson, *Trans. Faraday Soc.*, **49**, 1273 (1953).

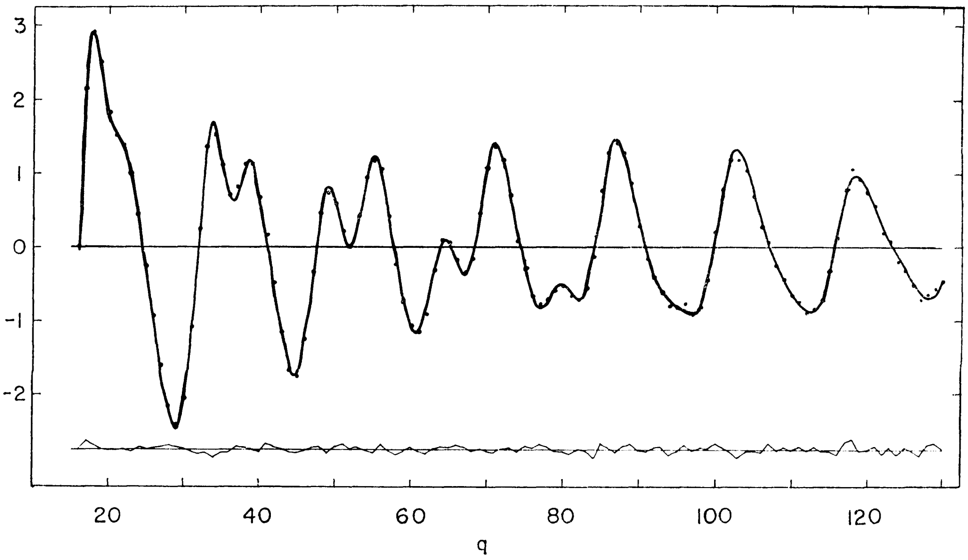

Fig. 1. Molecular intensity curves (dots for observed values and the solid curve calculated from the best-fit model) and the residuals (below).

Raman spectroscopy[12] were of comparable accuracy, nor were they free from the ambiguity due to the assumptions about the structural parameters. The present study aims to determine the structure of this molecule by electron diffraction in order to compare the C–C and C≡C bond distances with those in cyanogen and acetylene, respectively.

## Experimental

The sample of diacetylene (95% pure) purchased from Tokyo Kagaku Seiki Co. Ltd. was purified by vacuum distillation. An electron beam of the wavelength of about 0.06 Å, calibrated with reference to the $r_a$(C=O) distance of carbon dioxide[13] (1.1646 Å), was used to take diffraction photographs at room temperature (23°C) with the camera lengths of 107.79±0.02 mm and 243.23±0.02 mm. Photographic densities measured by a digital microphotometer were converted into electron intensities, from which reduced molecular intensities (Fig. 1) were obtained by a standard technique.[14] Other experimental details have been described elsewhere.[8,13] The radial distribution curve is shown in Fig. 2.

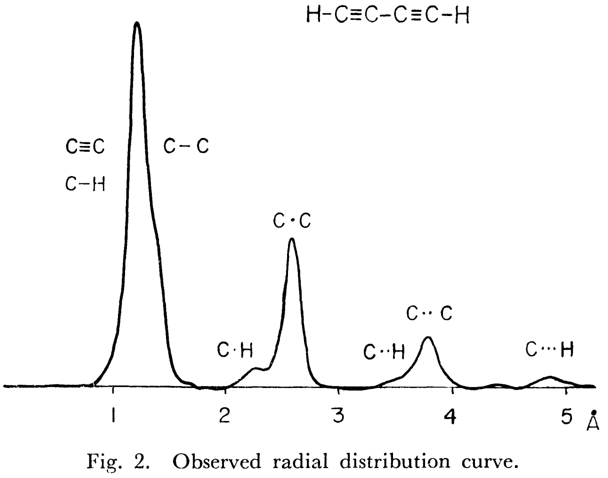

Fig. 2. Observed radial distribution curve.

## Analysis

The reduced molecular intensities were fitted to a theoretical expression using a least-squares method[15] with a diagonal weight function estimated from past experience. The $\kappa$ parameters representing asymmetric probability distributions for bonded pairs ($2.0\times10^{-5}$ Å$^3$ for C–H and $7\times10^{-7}$ Å$^3$ for C–C and C≡C) were estimated by a diatomic approximation.[16] The $\kappa$ parameters for nonbonded pairs were ignored. The mean amplitude and the distance for the H–H were fixed to their estimated values, because the contribution of this pair to the molecular intensity is insignificant. Tables 1, 2, and 3 list the $r_g$ distances,

Table 1. Observed internuclear distances[a]
(in Å units)

| | $r_g$ | | $r_g$ |
|---|---|---|---|
| C—H | $1.093_5\pm0.010$ | C · C | $2.587_4\pm0.002_5$ |
| C≡C | $1.217_6\pm0.001_4$ | C · · H | $3.63_0\ \pm0.03_3$ |
| C—C | $1.383_7\pm0.001_9$ | C · · C | $3.788_7\pm0.006_3$ |
| C · H | $2.27_8\ \pm0.01_5$ | C···H | $4.83_6\ \pm0.02_4$ |

a) Dots represent the number of atoms intervening each nonbonded atom pair. The uncertainties are estimated limits of error.

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12) J. H. Callomon and B. P. Stoicheff, *Can. J. Phys.*, **35**, 373 (1957).

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

14) Numerical experimental data of the leveled total intensity, the background function and the error matrix have been deposited with the Chemical Society of Japan (Document No. 7103). A copy may be secured by citing the document number and by remitting, in advance, ¥250 for photoprints. Payment by check or money order payable to: Chemical Society of Japan.

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

16) K. Kuchitsu, This Bulletin, **40**, 498, 505 (1967).

TABLE 2. OBSERVED AND CALCULATED MEAN AMPLITUDES (in Å units)

| | $l_{\mathrm{obsd}}$ | $l_{\mathrm{calcd}}$[a] | | |
|---|---|---|---|---|
| | | (a) | (b) | (c) |
| C≡C | $0.039_8 \pm 0.001_0$ | 0.0368 | (0.0368) | 0.0389 |
| C—C | $0.045_5 \pm 0.001_3$ | 0.0419 | (0.0419) | 0.0455 |
| C · C | $0.049_8 \pm 0.002_0$ | 0.0467 | 0.0569 | 0.0501 |
| C · · C | $0.061_3 \pm 0.004_5$ | 0.0514 | 0.0700 | 0.0579 |
| C—H | $0.085_5 \pm 0.005_5$ | 0.0741 | (0.0741) | 0.0855 |
| C · H | $0.09_7 \pm 0.01_2$ | 0.0794 | 0.0852 | — |
| C · · H | $0.10_7 \pm 0.03_3$ | 0.0840 | 0.0965 | — |
| C···H | $0.07_7 \pm 0.03_6$ | 0.0866 | 0.1060 | — |

a) Calculated values based on models (a), (b), and (c) discussed in the text: (a) harmonic parallel amplitudes, $\langle \Delta z^2 \rangle^{1/2}$, (b) rod model without bending-stretching interactions, (c) rod model with bending stretching interactions.

TABLE 3. OBSERVED AND CALCULATED SHRINKAGES (in Å units)

| | $\delta_{g\mathrm{obsd}}$ | $\delta_{g\mathrm{calcd}}$ | |
|---|---|---|---|
| | | (a) | (b) |
| C · H | $0.03_3 \pm 0.03$ | 0.020 | 0.021 |
| C · C | $0.014_1 \pm 0.002$ | 0.011 | 0.011 |
| C · · H | $0.06_4 \pm 0.03$ | 0.035 | 0.036 |
| C · · C | $0.030_2 \pm 0.006$ | 0.027 | 0.027 |
| C···H | $0.07_6 \pm 0.03$ | 0.054 | 0.056 |

(a), (b) See footnote a) of Table 2.

mean amplitudes and linear shrinkages, respectively, derived from the analysis.[14)] The uncertainties were estimated as 2.5 times the standard deviations with allowance for systematic errors (particularly, those in the scale factor for the distances and in the extraneous background for the mean amplitudes).[17)]

## Discussion

*Comparison of Bond Distances. C-C Single Bond*: The C-C bond distance ($r_g$) in diacetylene has been determined to be $1.387_7 \pm 0.001_9$ Å, about 0.007 Å shorter than in cyanogen[8)] ($1.390_8 \pm 0.002$ Å).[18)] This difference is analogous to, but much smaller than, that observed between the C-C distances in butadiene and glyoxal, 1.465±0.003 Å and 1.526±0.003 Å, respectively.[6)] As in that case, it seems possible to account for the observed difference at least qualitatively in terms of the difference in $\pi$ bond orders. According to a semiempirical estimate by the use of the Pariser-Parr-Pople method,[19)] the C-C $\pi$ bond order for diacetylene (0.4—0.5) appears to be slightly (of the order of a few hundredths) larger than that for cyanogen. The absolute magnitude of the estimated bond orders depends so sensitively on the empirical parameters assumed[7)] that a more elaborate treatment is necessary for a fully quantitative discussion. The C-C distance in diacetylene conforms to the Stoicheff rule,[4)] which predicts a "normal" ≡C-C≡ distance to be 1.379 Å.

*C≡C Triple Bond*: A significant difference has been observed between the C C bonds ($r_g$) in diacetylene ($1.217_6 \pm 0.001_4$ Å) and that in acetylene[20)]($1.212_2 \pm 0.001_0$ Å). There seems to be no previous experimental study in which confirmative evidence is given for a change in the triple-bond distance due to conjugation, whereas such a difference of the order of 0.005 Å or less is not unexpected[21)] from those in the $\pi$ bond orders (theoretical) and those in the C C stretching force constants (experimental). For instance, Julg and Pellégatti[22,23)] calculated the bond order of the diacetylene C C bond to be 1.906 or 1.888, which, together with their estimates of the gradient $\Delta r/\Delta p$, results in the difference in the C≡C bond distances of $0.122 \times (2-1.906) = 0.011_4$ Å or $0.130 \times (2-1.888) = 0.014_6$ Å, apparently larger than the experimental $r_g$ difference (~0.005 Å) given above.

*C-H Bond*: The C-H bond distance derived here ($r_g = 1.093_5 \pm 0.010$ Å) has much larger experimental error than those in the C-C distances. While this distance appears to be somewhat larger than those in acetylene[20)] ($r_g = 1.083_5 \pm 0.005_0$ Å) and in cyanoacetylene[12,24,25)] ($r_s = 1.0574$ Å, $r_0 = 1.057$ Å or 1.069 Å), the differences may be spurious, since they are within the limits of error; moreover, C-H distances are the most sensitive to the difference in the definition of distances.[26)]

*Effect of Bending Vibrations on Mean Amplitudes. Harmonic Parallel Amplitudes*: The observed mean amplitudes are compared in Table 2 with the mean parallel amplitudes, $\langle \Delta z^2 \rangle^{1/2}$, calculated by a conventional method[27,28)] (column a) using the quadratic force constants determined by Abe and Shimanouchi.[29)] For both bonded and nonbonded pairs the calculated parallel amplitudes are consistently smaller than the observed values. In particular, the observed CC amplitudes seem to have sufficient accuracy to investigate the origin of the "significant" discrepancies.

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[17)] The experimental errors in the distances and mean amplitudes have been estimated with particular caution, since appreciable differences were recognized between the observed and calculated mean amplitudes and rotational constants, as described in the discussion section.

[18)] The $r_g$(C-C) distance for cyanogen observed by electron diffraction, $1.392_5 \pm 0.002_2$ Å,[8)] has here been revised according to the recalibration of the scaler factor by the use of the infrared rotational constant, as described in Ref. 8.

[19)] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953); J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

[20)] Y. Morino, K. Kuchitsu, T. Fukuyama, and M. Tanimoto, *Acta Crystallogr.*, **A25**, S127 (1969); Y. Morino, K. Kuchitsu, and M. Tanimoto, to be published.

[21)] D. R. Lide, Jr., *Tetrahedron*, **17**, 125 (1962).

[22)] A. Julg and A. Pellégatti, *Theor. Chim. Acta*, **2**, 202 (1964).

[23)] A. Pellégatti, Thesis, Marseille (1967).

[24)] A. A. Westenberg and E. B. Wilson, *J. Amer. Chem. Soc.*, **72**, 199 (1950).

[25)] C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).

[26)] K. Kuchitsu, *ibid.*, **49**, 4456 (1968).

[27)] Y. Morino, K. Kuchitsu, and T. Shimanouchi, *ibid.*, **20**, 726 (1952).

[28)] S. J. Cyvin, "Molecular Vibrations and Mean Square Amplitudes", Universitetsforlaget, Oslo and Elsevier, Amsterdam (1968).

[29)] K. Abe and T. Shimanouchi, to be published.

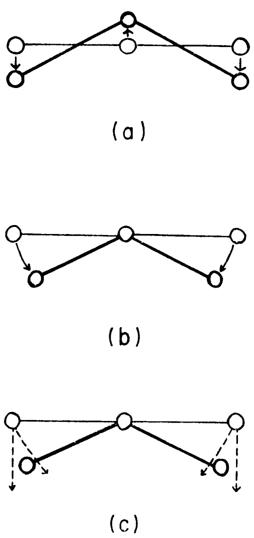

Fig. 3. The loci of the atoms in the bending vibration of a triatomic system: (a) normal coordinates of bending, (b) rod model without bending-stretching interaction, (c) bending-stretching interaction with a positive $\alpha$ parameter is included.

The conventional method ignores the effect of bending vibrations (perpendicular to the equilibrium molecular axis, Fig. 3a) on the displacements of internuclear distances, and the bond-stretching vibrations (parallel to the axis) are assumed to be "harmonic" (here called model a). However, since the present molecule has a low-frequency bending vibration ($\nu_9=222$ cm$^{-1}$),[30] the stretching displacements should depend appreciably on the bending displacements, and the above approximations may not be valid.

*Effect of Bending without Bend-Stretch Interaction*: A simple approach to this problem is to assume model b, where the bonds retain their "average" distances in the bending displacements[31-33] (Fig. 3b). The potential function is assumed to have no third-order term proportional to $\Delta r\cdot\phi^2$, which represents the interaction between the stretching and bending displacements. Accordingly, the probability distribution function of a bond distance, $P(r)$, which has a Gaussian form with a slight distortion due to the stretching anharmonicity, is assumed to be independent of the bending displacements.[34]

If one expands an instantaneous distance $r$ (bonded or nonbonded) in terms of the Cartesian displacements parallel and perpendicular to the equilibrium molecular axis, $\Delta z$ and $\Delta\rho$, respectively, one gets[16,35]

$$\begin{aligned} r &= r_e+\Delta r \\ &= r_e+\Delta z+\frac{\Delta\rho^2}{2r_e}-\frac{\Delta z\Delta\rho^2}{2r_e^2}+\frac{\Delta z^2\Delta\rho^2}{2r_e^3}-\frac{\Delta\rho^4}{8r_e^3}+\cdots \end{aligned} \tag{1}$$

where $\Delta\rho^2=\Delta x^2+\Delta y^2$. The mean-square amplitude reckoned from the $r_g$ distance is given by

$$\begin{aligned} l_g^2 &= \langle r^2\rangle-\langle r\rangle^2 = \langle\Delta z^2\rangle-\langle\Delta z\rangle^2 \\ &\quad+\frac{1}{r_e}(\langle\Delta z\Delta\rho^2\rangle-\langle\Delta z\rangle\langle\Delta\rho^2\rangle)+\frac{1}{r_e^2}\Bigg[\frac{1}{4}(\langle\Delta\rho^4\rangle \\ &\quad-\langle\Delta\rho^2\rangle^2)-(\langle\Delta z^2\Delta\rho^2\rangle-\langle\Delta z\rangle\langle\Delta z\Delta\rho^2\rangle)+\cdots \end{aligned} \tag{2}$$

where the carets denote thermal averages. Since the molecule is linear in equilibrium, the Cartesian displacements for a nonbonded pair are simply the sums of the corresponding displacements for the component bonded pairs. For instance, a parallel displacement for a nonbonded *i-k* pair in a linear *i-j-k* arrangement is given by

$$\Delta z_{ik} = \Delta z_i-\Delta z_k = \Delta z_{ij}+\Delta z_{jk} \tag{3}$$

The parallel displacement for a bonded pair, on the other hand, is related to the bond-stretching displacement, $\Delta r$, and the perpendicular displacement,

$$\Delta z(\text{bond}) = \Delta r-\frac{\Delta\rho^2}{2r_e}+\frac{\Delta r\Delta\rho^2}{2r_e^2}-\frac{\Delta\rho^4}{8r_e^3}-\frac{\Delta r^2\Delta\rho^2}{2r_e^3}+\cdots \tag{4}$$

Since the contribution from the second (negative) term is important, the mean projected displacement $\langle\Delta z$ (bond)$\rangle$ is usually much smaller than $\langle\Delta r\rangle$ and is sometimes negative.[16,36]

According to the present assumption, $\Delta r$ and $\Delta\rho^2$ are independent of each other, and the $\Delta r$ for a bond is equal to the $\Delta z$ for a linear structure without bending displacements. The latter can be expressed as a linear combination of the $\Sigma$-type normal coordinates ($Q_1$ through $Q_5$) with their coefficients $a_i$ determinable from a conventional normal-coordinate analysis,[37]

$$\Delta r = \sum_{i=1}^{5} a_i Q_i \tag{5}$$

The perpendicular displacement, $\Delta\rho^2$, can be calculated in a similar way from the $\Delta x$ and $\Delta y$, which are linear functions of the $\pi$-type coordinates, $Q_6$ through $Q_9$.

The mean amplitudes for nonbonded pairs calculated by this model, listed in column b of Table 2, are appreciably larger than those based on model a, where all the $\Delta\rho$ displacements in Eqs. (2) and (4) are equal to zero. The observed CC amplitudes lie between a and b, indicating that the latter model overestimates the effect of bending vibrations. Hence, a bending-stretching interaction ought to be introduced in order to attain a better agreement. (See next subsection.)

*Shrinkage Effects*: The shrinkage[35] calculated by the models a and b are nearly equal, as listed in Table 3. The shrinkage depends essentially on the perpendicular displacements alone and is independent of whether the atoms take rectilinear or curvilinear loci shown in Fig. 3a and 3b, respectively.[35]

*Rotational Constants*: The $r_g$ distances determined in the present study have been converted into the $r_\alpha{}^0$ distances by the equation, which is based on model b,[26,38]

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30) F. A. Miller, D. H. Lemmon, and R. S. Witkowski, *Spectrochim. Acta*, **21**, 1709 (1965).

31) L. S. Bartell, *J. Chem. Phys.*, **38**, 1827 (1963).

32) M. A. Pariseau, I, Suzuki, and J. Overend, *ibid.*, **42**, 2335 (1965).

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

34) M. Tanimoto, K. Kuchitsu, and Y. Morino, *ibid.*, **43**, 2776 (1970).

35) Y. Morino, J. Nakamura, and P. W. Moore, *J. Chem. Phys.*, **36**, 1050 (1962).

36) K. Kuchitsu, This Bulletin **44**, 96 (1971).

37) E. B. Wilson, Jr., J. C. Decius and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York (1955).

38) K. Kuchitsu and S. Konaka, *J. Chem. Phys.*, **45**, 4342 (1966).

TABLE 4. AVERAGE STRUCTURE AND ROTATIONAL CONSTANTS

| | | Obsd | Calcd[a] | |
|---|---|---|---|---|
| | | | (b) | (c) |
| $r_g - r_\alpha{}^0$ (Å) | C—H | — | 0.0038 | 0.0113 |
| | C≡C | — | 0.0062 | 0.0078 |
| | C—H | — | 0.0288 | 0.0328 |
| $B_0$ ($\mathrm{cm}^{-1}$) | | 0.14638±0.0001[b]<br>0.14641±0.00013[c]<br>0.14689±0.00004[d] | 0.1453±0.0003 | 0.1464 |

a) Calculated by models (b) and (c) respectively. See text and footnote a) of Table 2.
b) Infrared, Ref. 10. c) Infrared, Ref. 11. d) Rotational Raman, Ref. 12.

$$r_\alpha{}^0 = r_g - \frac{3}{2}a(\langle\Delta z^2\rangle_T - \langle\Delta z^2\rangle_0) - \langle\Delta\rho^2\rangle_0/2r_e - \delta r \qquad (6)$$

where the centrifugal corrections,[39] $\delta r$, are less than $10^{-4}$ Å for all the bonded pairs. The corrections for the $r_g$ to $r_\alpha{}^0$ conversion[40], listed in Table 4 column b, are significant, since they exceed the experimental error of $r_g$.

The rotational constant for the ground vibrational state, $B_0$, has been calculated from the $r_\alpha{}^0$ parameters on the assumption that the correction from $B_z$ ($\approx B_\alpha{}^0$)[37] to $B_0$ conforms to the ordinary second-order formula[41,42] based on infinitesimal vibrational amplitudes. This correction, being proportional to $B^2$, is trivial for this molecule ($-8\times10^{-5}$ $\mathrm{cm}^{-1}$).

The rotational constant estimated in this way, $B_0$(ED)$=0.1453\pm0.0003$ $\mathrm{cm}^{-1}$, is significantly different from any of the spectroscopic values given in Table 4. The infrared values are presumably more accurate than the Raman value, since in the latter experiment the rotational analysis may have been biased by overlapping hot bands, as was pointed out by Maki[9] in the case of cyanogen.

The discrepancy is probably originated, at least in part, in the $B_0$(ED), which is based on model b for the $r_g$ to $r_z$ conversion. A possible systematic error due to this model has not been counted in the uncertainty given above. A further study in this regard is made in the next subsection.

While the basic scheme of coordinating the average structure derived from electron diffraction and spectroscopy seems to work for a number of nonlinear polyatomic molecules with small vibrational amplitudes,[26,38] a special formalism is required for a calculation of the ground-state rotational constant for a molecule with large-amplitude vibrations (in particular, for a quasilinear molecule) from a given set of thermal-average distances.[43] None of such a treatment has been made in the present study.

*Bend-Stretch Interactions.* The discrepancies observed in the mean amplitudes and in the rotational constant discussed above indicate the presence of appreciable contributions from bending-stretching interactions left out in the calculations. Suppose a displacement $\Delta r$ in Eq. (4) increases with the bending displacement $\Delta\rho^2$ so as to partially compensate for the second term, $-\Delta\rho^2/2r_e$, and the atoms take loci shown in Fig. 3c. Then the mean amplitude should fall in between (a) and (b) of Table 2, and the effective $B_0$ (ED) should increase. One may thus assume a model c, where the displacement of a bond $j$ is given, in place of Eq. (5), as

$$\Delta r_j = \sum_{i=1}^{5} a_i Q_i + \alpha_j(\phi_j{}^2 + \phi_j{}'^2) \qquad (7)$$

where $\alpha_j$ is a positive constant. The angles of bending from $\pi$ on both ends of the bond $j$, $\phi_j$ and $\phi_j{}'$, can be expanded in terms of the normal coordinates $Q_6$ through $Q_9$.

The physical significance of a positive parameter $\alpha_j$ is to introduce into the potential function a negative third-order term, $-\alpha_j f_j \Delta r_j(\phi_j{}^2+\phi_j{}'^2)$, where $f_j$ is a second-order force constant for the bond stretching. For a number of linear molecules ($CO_2$,[32,33] $CS_2$,[32,33] OCS,[44] HCN(DCN),[45] NNO,[46] $C_2H_2(C_2D_2)$[47]), where precise values of third-order potential constants are known from spectroscopic experiments, the constants representing the bending-stretching interaction of this sort are all *negative* (of the order of a few tenths of one mdyn). Furthermore, the $\pi$ bond order of the C–C single bond in diacetylene is expected to decrease with the C≡C–C bending displacements as a result of the decrease in the degree of conjugation, and this effect should make an appreciable positive contribution to $\alpha_{C-C}$. The corresponding (probably negative) contribution to $\alpha_{C\equiv C}$ seems to be much less important, since the difference in the C≡C bond distances in diacetylene and acetylene is found in the present study to be only about 0.005 Å.

It has been shown, on an empirical basis, that the following set of bending-stretching interactions makes the bonded and nonbonded CC mean amplitudes agree with the observed values as listed in Table 2, column (c):

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[39] M. Iwasaki and K. Hedberg, *J. Chem. Phys.* **36**, 2961 (1962).

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

[41] D. R. Herschbach and V. W. Laurie, *ibid.*, **37**, 1668 (1962).

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

[43] J. T. Hougen P. R. Bunker, and J. W. C. Johns, *ibid.*, **34**, 136 (1970).

[44] T. Nakagawa and Y. Morino, *ibid.*, **26**, 496 (1968).

[45] T. Nakagawa and Y. Morino, This Bulletin, **42**, 2212 (1969).

[46] I. Suzuki, *J. Mol. Spectrosc.* **32**, 54 (1969).

[47] I. Suzuki and J. Overend, *Spectrochim. Acta*, **25A**, 977 (1969); I. Suzuki, private communication, 1970.

$\alpha_{\mathrm{C-C}}=0.352$ Årad$^{-2}$, $\alpha_{\mathrm{C\equiv C}}=0.152$ Årad$^{-2}$,

and $\alpha_{\mathrm{C-H}}=0.599$ Årad$^{-2}$.

In addition, the $r_g-r_\alpha^0$ corrections based on this set are shown to result in the $B_0$ (ED) in excellent accord with the $B_0$(infrared) as listed in Table 4.

The present model c should be taken with reservation, in spite of the above virtual success, since the bending-stretching interactions given above seem to be larger than those expected for ordinary linear molecules, even if the influence of the conjugation in diacetylene is taken into account. The above $\alpha$ parameters are subject to a further examination with suspicion of systematic errors.

Such a strong bending-stretching interaction, if present, poses a problem in the comparison of bond distances in different molecules. A usual scheme of comparison in terms of the average bond distances, where the difference in the $r_g$ distances is regarded as a good representation of that in the $r_e$ distances,[26] is no longer valid for a group of molecules with very different $\alpha$ parameters. Future systematic studies of the structures of linear conjugated molecules will present a clue to the solution of this problem.