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Bond Lengths of Dimethylacetylene as Determined by Gas Electron Diffraction

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The bond distances of dimethylacetylene have been determined by electron diffraction to be r_g(C–C)$=1.467_5\pm0.001_3$ Å, r_g(C≡C)$=1.213_5\pm0.001_3$ Å, r_g(C–H)$=1.115_8\pm0.005_9$ Å, and ∠C–C–H$=110.7\pm0.4°$, the uncertainties representing the limits of experimental error. The carbon-carbon single bond length has been found to be in good agreement with that in butadiene, as was qualitatively to be expected from Stoicheff's empirical rule. The carbon-carbon triple bond length appears to be longer than that of acetylene and shorter than that of diacetylene by a few thousandths of an angstrom. The dependence of the triple-bond lengths on the environment is discussed in terms of the change in conjugation and hyperconjugation.

Abundant experimental data from spectroscopy and electron diffraction accumulated over three decades are of basic importance to a systematic understanding of molecular structure. A marked dependence of the carbon-carbon single bond lengths on environment was first recognized by Herzberg *et al.*[1] in 1937. A distinct but less conspicuous difference in C=C double bond lengths in allene and ethylene was later shown by Overend and Thompson.[2] A subsequent analysis of the available data led Stoicheff[3] to determine empirical regularities for the "normal" behavior of C–C and C=C bond lengths, which vary nearly linearly with the number of atoms attached to the carbon atoms in question. While a majority of the C–C and C=C lengths in hydrocarbons seem to follow his rule to 0.005 Å, this does not necessarily preclude an appreciable deviation due to adjacent heteroatoms, *i.e.*, a "secondary" effect, about which little is known at present. Recently a series of molecules with C–C bonds adjacent to two double bonds (butadiene, acrolein and glyoxal) were studied by Kuchitsu, Fukuyama, and Morino,[4] who demonstrated a systematic variation of the single-bond lengths. A similar difference was observed in the C–C bonds adjacent to two triple bonds (cyanogen[5] and diacetylene[6]). The purpose of the present study is to extend such investigations to C≡C triple-bond systems.

The lengths of ordinary C≡C bonds have been supposed to be insensitive to their environment. For example, the C≡C lengths (r_0) in acetylene, methylacetylene, and cyanoacetylene were found to be nearly equal (1.207 Å),[7] so that any increase in the length due to conjugation or hyperconjugation should be extremely small (probably not over 0.005 Å),[8] whereas Stoicheff remarked a slight decrease when halogen atoms were adjacent to a C≡C bond.[3] The constancy of the C≡C length

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

[2] J. Overend and H. W. Thompson, *J. Opt. Soc. Am.*, **43**, 1065 (1953).

[3] B. P. Stoicheff, *Tetrahedron*, **17**, 135 (1962).

[4] K. Kuchitsu, T. Fukuyama and Y. Morino, *J. Mol. Structute*, **1**, 463 (1968).

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

[6] Y. Morino, K. Kuchitsu and M. Tanimoto, to be published.

[7] G. Herzberg and B. P. Stoicheff, *Nature*, **175**, 79 (1955).

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

has had practical utility in the spectroscopic determination of molecular structure; when the number of independent structural parameters exceeded that of rotational constants available, the r_0(C≡C) length has often been set equal to that in simple acetylenic compounds, say, 1.206 Å, since this assumption was one of the most plausible. The r_s(C≡C) distances in a number of molecules measured by Costain and others seem to offer further support for this invariance, since they range from 1.205 Å (cyanoacetylene)[9] to 1.209 Å (tert-butylacetylene).[10]

However, if one intends to study the dependence of the bond lengths on the environment more carefully (say, with an accuracy better than 0.005 Å), one has to investigate the equilibrium or average distances instead of the r_0 or r_s distances. Since the latter parameters for polyatomic molecules are based on only operational definitions, they are not always suitable for such a critical comparison of bond lengths.

In this connection, the structure of diacetylene was examined in our laboratory. The *thermal average* C≡C length determined by electron diffraction was found to be $r_g(\text{C≡C})=1.217_6\pm0.001_4$ Å,[6] about 0.006 Å longer than the corresponding value in in acetylene, $r_g(\text{C≡C})=1.212\pm0.001$ Å.[6] This suggests that the *equilibrium* bond lengths (r_e) also differ by a similar amount, so that a further experimental study of molecules with C≡C bonds seems to be worthwhile.

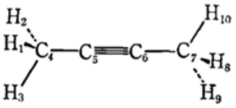

Fig. 1. The structure and numbering convention of dimethylacetylene.

The bond lengths in dimethylacetylene (2-butyne) have been investigated by gas electron diffraction in the present study. The structure of this molecule was first studied by means of electron-diffraction measurements by Pauling *et al.*,[11] who gave r(≡C–C≡)$=1.47\pm0.02$ Å on the assumptions that the other bond lengths were r(C≡C)$=1.20$ Å and r(C–H)$=1.09$ Å. The rotational constant, B_0, was determined by Callomon and Stoicheff[12] on the basis of an analysis of their pure rotational Raman spectrum. They could not, however, determine the dimensions of dimethylacetylene since they obtained the B_0 constant of the normal species alone. From a comparison of the observed moment of inertia with that calculated from the methylacetylene parameters, which was significantly smaller than the observed value, they concluded that at least one of the carbon-carbon bonds was longer than in the closely related molecule, methylacetylene.

Experimental

Two millilitres of a 99% pure liquid sample of dimethylacetylene were purchased from the Tokyo Kagaku Seiki Co., Ltd., and were used after vacuum distillation. Diffraction photographs were taken at room temperature using an apparatus with an r^3-sector.[13] The accelerating voltage (about 40 kV), stabilized to within 0.01%, was monitored during the exposure and was further calibrated with reference to the C=O length of carbon dioxide.[5] Four plates were chosen from each camera distance (107.78±0.02 mm or 243.23±0.02 mm), and their photographic densities, measured by a microphotometer, were analyzed in order to obtain the molecular intensities.

Analysis

The molecular intensities were analyzed by a conventional least-squares method[14] with some modifications.[4] The alterations involved a choice of independent parameters and corrections for vibrational effects. The calculations were made by using the HITAC 5020E at the Computer Centre of the University of Tokyo.

As a result of molecular vibration, the r_g distances determined by electron diffraction are not additive. The so-called shrinkage effect[15] should disappear in regard to the r_α distances, which are obtained from r_g by subtracting the perpendicular and centrifugal contributions:[16]

$$r_\alpha = r_g - \frac{\langle \Delta\rho^2\rangle}{2r_e} - \delta r. \tag{1}$$

Since the r_α structure represents the thermal-average positions of constituent atoms,[4] it corresponds to the equilibrium symmetry of the molecule. In other words, provided the molecular symmetry is known from spectroscopy, the number of distance parameters (r_α) can be decreased by assuming the symmetry as a constraint. In the present analysis, the bond lengths, r(C–H), r(C–C) and r(C≡C), and the angle θ(CCH) with regard to the r_α structure were taken as independent parameters.

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

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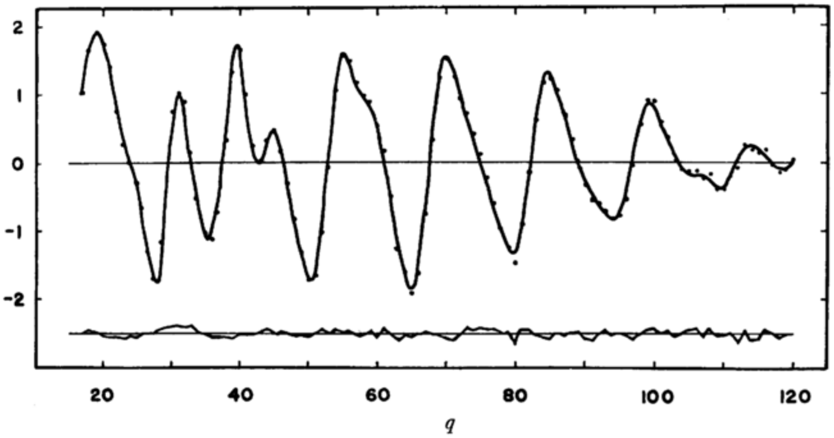

Fig. 2. Reduced molecular intensity curves (dots for observed values and the solid curve calculated from the best-fit model) and the residuals (below)

Since longer nonbonded H···H atom pairs contribute only a negligible amount to the reduced molecular intensity in the observed q range, the reduced molecular intensity is insensitive to the internal rotation of the methyl groups. Since the infrared spectra lead us to believe that the two methyl groups undergo a nearly free internal rotation,[17] the present analysis was based on the assumption of free rotation.

The asymmetry parameters, κ, were calculated by the diatomic approximation[18] to be 2.0×10^{-5} Å^3 for the CH bonded pairs and 8×10^{-7} Å^3 for the C≡C and C–C bonded pairs. The parameters for the other atom pairs were ignored since their effects were unimportant.

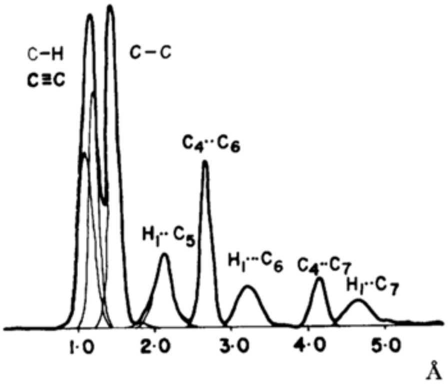

Fig. 3. Radial distribution curve. The atom pairs contributing to individual peaks are shown.

TABLE 1. BOND LENGTHS AND BOND ANGLE IN DIMETHYLACETYLENE[a)]

	r_a	$r_\alpha{}^0$	r_g	Limits of error
C–H	1.099_7	1.102_3	1.115_8	0.005_9 Å
C–C	1.458_9	1.462_7	1.467_5	0.001_3
C≡C	1.206_3	1.208_2	1.213_5	0.001_3
θ(CCH)	110.7°			0.4°

a) See Eqs. (1) and (2) for the definition of distances.

TABLE 2. COMPARISON OF OBSERVED MEAN AMPLITUDES WITH CALCULATED VALUES (in Å units)

Atom pair[a)]	l_{obsd}	l_{calcd}
C_4–H_1	$0.073_0\pm0.002_3$	0.0784
C_5≡C_6	$0.035_2\pm0.002_8$	0.0365
C_4–C_5	$0.046_7\pm0.001_7$	0.0467
H_1•H_2	0.1260 (fixed)	0.1260
H_1•C_5	$0.100_7\pm0.005_1$	0.1062
C_4•C_6	$0.052_8\pm0.002_0$	0.0510
H_1••C_6	$0.122_6\pm0.009_7$	0.1301
C_4••C_7	$0.061_2\pm0.007_2$	0.0593
H_1•••C_7	$0.13_8\ \pm0.01_7$	0.1461

a) See Fig. 1 for the numbering of the atoms.

Table 1 lists the values of independent parameters obtained in the above analysis, together with their estimated limits of error (2.5 times the random standard errors plus systematic errors). The observed mean amplitudes given in Table 2 agree with the parallel amplitudes calculated by a conventional method[19] within the range of experimental error.

Discussion

Average Structure. The distances between the atoms in the vibrational ground state, $r_\alpha{}^0$, were

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[17] D. Papoušek, J. Adams and K. N. Rao, Symposium on Molecular Structure and Spectroscopy O6, Columbus, Ohio, 1968.

[18] K. Kuchitsu, This Bulletin, **40**, 498 (1967).

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

obtained from the r_α distances by:[20]

$$r_\alpha{}^0 = \lim(T \rightarrow 0°\mathrm{K})r_\alpha = r_\alpha - (\langle \Delta z \rangle_{\mathrm{T}} - \langle \Delta z \rangle_0), \qquad (2)$$

where $\langle \Delta z \rangle = \langle \Delta r \rangle - (\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle)/2r_e$. The $\langle \Delta r \rangle$ term was calculated by assuming a Morse-type potential function for a bond, the anharmonicity parameter being taken from the corresponding diatomic molecule. The generalized mean amplitudes, $\langle \Delta x^2 \rangle$, $\langle \Delta y^2 \rangle$, and $\langle \Delta z^2 \rangle$, were calculated by the use of the quadratic force constants.[21] The values of the $r_\alpha{}^0$ distances are given in Table 1.

The rotational constant, B_z, calculated from the $r_\alpha{}^0$ structure was compared with the ground-state rotational constant, B_0, by correcting for vibration-rotation interactions.[20] The correction, -3×10^{-5} cm^{-1}, was an order of magnitude smaller than the experimental error. The rotational constant, B_0, calculated from the diffraction structure was 0.1116 ±0.0002 cm^{-1}, which was 0.5±0.2% smaller than the spectroscopic B_0 constant,[12] 0.1122±0.0002 cm^{-1}.

This difference is probably due to the systematic error in the rotational-Raman measurement, since, for similar molecules[22-25] listed in Table 3, the rotational constants obtained from the Raman spectra are about 3×10^{-4} cm^{-1} larger than those derived from the infrared spectra, the difference exceeding their limits of error. The origin of the discrepancy for cyanogen was ascribed by Maki[26] to the Raman measurement biased by overlapping lines due to molecules in the low-lying vibrational excited states. If this is also the case for dimethylacetylene, a proper spectroscopic B_0 value should be smaller than the observed value[12] by about 5×10^{-4} cm^{-1}; it is thus estimated to be 0.1117±0.0002 cm^{-1}, in reasonable agreement with the present diffraction result.

TABLE 3. ROTATIONAL CONSTANTS B_0 DERIVED FROM RAMAN AND INFRARED SPECTROSCOPY (in cm^{-1} units)

	Rotational Raman	Ref.	Infrared	Ref.	Δ[a]	ν[b]
C_2H_2	1.1769	12	1.17660	24	3	625.6
C_2N_2	0.15752	22	0.15712	26	4	233
$H_2C{=}C{=}CH_2$	0.2965_3	23	0.29632	25	2_1	354
C_4H_6	0.1122	12	(0.1117)[c]		5[c]	194

a) Difference in B_0 : B_0(RR)$-B_0$ (IR) (in 10^{-4}cm^{-1} units).
b) Frequency of the lowest bending vibration.
c) Estimated.

Comparison of Bond Lengths. As was recently discussed by Kuchitsu,[27] distance parameters can be compared most conveniently in terms of the thermal-average (r_g) distances, since the differences in r_g for analogous molecules correspond to those in r_e within the range of experimental error; the effect of thermal vibration (r_g-r_e) on a certain bond distance should be essentially equal to its counterparts for analogous molecules. The r_g parameters determined above afford a clue to the problem set up in the introduction, *i. e.*, the effect of the environment on carbon-carbon triple and single bond lengths.

The change in multiple bond lengths by conjugation has been discussed from a theoretical point of view. Mulliken[28] argued that the multiple-bond length should increase only slightly since π-electrons delocalized into adjacent bonds as a result of conjugation should return to the original bonds because of mutual repulsion. In consideration of the effects of hybridization and electron delocalization on the CC bond lengths, Bak and Hansen-Nygaard[29] estimated a multiple-bond lengthening of a few thousandths of an angstrom from the corresponding shortening of the neighboring bonds. A number of experimental data indicating such lengthenings in multiple-bonds were given; those data were in rough agreement with what they expected. At the same time, however, they stressed the usefulness of further, more accurate experiments in order to make the structure comparison less ambiguous.

The present study has confirmed that the C≡C bond length in dimethylacetylene is significantly shorter than that in diacetylene[6] and longer than that in acetylene[6] (Table 4). Furthermore, the value for dimethylacetylene is in good agreement with the bond length in vinylacetylene.[30] The

TABLE 4. COMPARISON OF CARBON-CARBON TRIPLE BOND LENGTHS (in Å units)

Molecule		r_g (C≡C)
Acetylene	HC≡CH	1.212 ±0.001
Dimethylacetylene	CH_3–C≡C–CH_3	1.213_5±0.001_3
Vinylacetylene	CH_2=CH–C≡CH	1.215 ±0.003
Diacetylene	HC≡C–C≡CH	1.217_6±0.001_4

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20) K. Kuchitsu and S. Konaka, *ibid.*, **45**, 4342 (1966).
21) K. Abe and T. Shimanouchi, to be published. The authors are indebted to their information prior to publication.
22) C. K. Møller and B. P. Stoicheff, *Can. J. Phys.*, **32**, 635 (1954).
23) B. P. Stoicheff, *Can. J. Phys.*, **33**, 811 (1955).
24) W. J. Lafferty and R. J. Thibault, *J. Mol. Spectry.*, **14**, 79 (1964).
25) A. G. Maki and R. A. Toth, *ibid.*, **17**, 136 (1965).
26) A. G. Maki, *J. Chem. Phys.*, **43**, 3193 (1965).
27) K. Kuchitsu, *ibid.*, **49**, 4456 (1968).
28) R. S. Mulliken, *Tetrahedron*, **6**, 68 (1959).
29) B. Bak and L. Hansen-Nygaard, *J. Chem. Phys.*, **33**, 418 (1960).
30) T. Fukuyama, K. Kuchitsu and Y. Morino, This Bulletin, **42**, 379 (1969).

above results are consistent with simple intuition in terms of the effect of conjugation and hyperconjugation on bond lengths. According to Mulliken,[31] the effect of conjugation should be larger than that of hyperconjugation. Thus, the C≡C distance in dimethylacetylene should fall in between those of diacetylene and acetylene. For a number of other molecules the lengths of CC triple bonds have been reported in terms of r_s distances. (For example, see Ref. 9). Presumably the r_s(C≡C) distances are shorter than the r_g(C≡C) distances by a few thousandths of an angstrom.

The C–C distance (r_g) determened in this study, $1.467_5 \pm 0.001_3$ Å, is equal to that in butadiene[32] (r_g(C–C)$=1.465\pm0.003$ Å) within the range of experimental uncertainty. This observation agrees qualitatively with Stoicheff's rule, which says they should be identical. The C–C bond length in methylacetylene is also expected to be similar to those in dimethylacetylene and butadiene, whereas the r_s(C–C) distance was reported by Costain[9] to be 1.4589 Å. An electron-diffraction study of this molecule is now in progress.

The r_g(C–H) distance determined above (r_g(C–H)$=1.115_8\pm0.005_9$ Å) seems to be slightly longer than the CH bond length in ethane (r_g(C–H)$=1.110_8\pm0.002$ Å[27,33]), but the large limit of error attached to the former bond length forbids a quantitative comparison. The CCH angle in dimethylacetylene, 110.7±0.4°, appears to be only slightly smaller than that in ethane[27] (111.5±0.3°). A similar value has been reported for methylacetylene[9] (110.2° in r_s structure).

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[31] R. S. Mulliken, *Tetrahedron*, **17**, 247 (1962).

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

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