An Electron Diffraction Investigation of the Molecular Structure of 1,4-Dichlorobutyne. I. Determination of Bond Distances and Angles*

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1. Introduction

Thermodynamic measurements have shown that the C—C≡C—C axis in dimethylacetylene has no appreciable restriction on the internal rotation of the two end groups around this axis[1-3]. One is thus led to an expectation that the hindering barriers for substituted dimethylacetylene molecules would be much lower than that for the corresponding ethane derivatives, because the distance of the groups in the former is much longer than that in the latter. This has been confirmed by the measurement of the dipole moment of 1,4-dichloro-2-butyne, $ClCH_2-C\equiv C-CH_2Cl$[4,5].

This molecule seems to stimulate an electron diffraction investigation, because a heavy chlorine atom with a relatively large scattering power is included in each rotating group, so that the diffraction pattern will give us some information of the potential barrier; in addition, there have been reported very few electron-diffraction studies on the internal rotation of the molecules whose potential barriers are relatively low[6].

It is of particular importance to determine the C—Cl bond distances of this molecule. Pauling and his coworkers[7] found, by using visual electron diffraction data, that the C—Cl bond distance in propargyl chloride, $H-C\equiv C-CH_2Cl$, is 1.82± 0.02Å. This result is very striking, for it is well known that the carbon-chlorine bond distances in most chlorinated hydrocarbon molecules[8] are about 1.77Å ("normal" C—Cl bond distance), or shorter

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* Presented at the Eighth Annual Meeting of the Chemical Society of Japan, April, 1955.

[1] B. L. Crawford, Jr. and W. W. Rice, *J. Chem. Phys.*, **7**, 437 (1939).

[2] G. B. Kistiakowsky and W. W. Rice, ibid., **8**, 618 (1940).

[3] D. W. Osborne, C. S. Garner and D. M. Yost, ibid., **8**, 131 (1940).

[4] Y. Morino, I. Miyagawa, T. Chiba and T. Shimozawa, This Bulletin, **30**, 222 (1957).

[5] Y. Morino, I. Miyagawa and A. Wada, *J. Chem. Phys.*, **20**, 1976 (1952).

[6] For example Si_2Cl_6, (K. Yamasaki, et al., *J. Chem. Soc. Japan*. **69**, 104 (1948); D. A. Swick and I. L. Karle, *J. Chem. Phys.*, **23**, 1499 (1955)). See also Ref. 24.

[7] L. Pauling, W. Gordy and J. H. Saylor, *J. Am. Chem. Soc.*, **64**, 1753 (1942).

[8] P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).

(e. g., 1.72Å in C_2Cl_4)[9], and we have seldom found molecules whose C−Cl bond distances are longer than 1.80Å[10,11]. If this abnormal increase is based on a special property of $-C{\equiv}C-CH_2Cl$ group, then it may be of interest to decide whether the C−Cl bond in $ClCH_2-C{\equiv}C-CH_2Cl$ molecule is longer than the "normal" distance or not. Furthermore, various data on C≡C−C system[12−14] show that the C−C bond distance adjacent to a triple bond is about 1.46Å, much shorter than its normal value, and is nearly constant. Therefore, it is also desirable to determine the C−C bond distance accurately and to compare it with the known results.

The subject of this article is the determination of the bond distances and angles of this molecule by the electron diffraction method with a view to apply this structural information as basic data for the study of internal rotation in this molecule, which will be discussed in the following article[15].

2. Experimental[16]

The electron diffraction instrument used in this investigation which incorporates a rotating sector was designed by Morino, Kimura and Iwasaki[17]. The apparatus is essentially similar to that constructed by Ino[18].

Diffraction photographs were obtained on Fuji Process Hard Plates with an r^2-sector, which was placed 23.7 mm. from the photographic plate and was rotated rapidly during exposure. A camera length was either 11.82 cm. or 27.91 cm., to cover the angular range of 15 to 90, and 5 to 27 in q units, respectively. The accelerating voltage of the electron source was regulated to within 0.1 percent., and the electron beam was focused on the photographic plate to a point about 0.1 mm. in diameter. The wavelength of the electron was determined to be 0.0565Å by measuring the transmission patterns of gold foil.

1, 4-Dichloro-2-butyne was prepared by T. Shimozawa of our laboratory from 2-butyne-1, 4-diol and thionyl chloride[19], the boiling point being 62–64°C at 18 mmHg. The sample was introduced into the electron beam through a fine nozzle by heating to about 40°C[20]. The nozzle was surrounded by a liquid air trap to prevent the sample from diffusing through the camera. A set of two photographs were taken with consecutive exposures of 1/2 and 1 min. which were later used for density-intensity calibration[21]. The patterns were scanned by a Riken B-type recording microphotometer to measure the optical density as a function of the radius[22]. The photographic plates were rotated rapidly about the center of the diffraction pattern while being scanned by the microphotometer.

Optical densities were converted in to relative intensities by Karle's procedure[21]. The scattering intensity curve obtained with a short camera length was corrected to eliminate a small amount of extraneous scattering. A smooth background line was drawn through the intensity curve multiplied by q(L=11.82 cm.) or $q^{1/2}$(L=27.91 cm.), and the molecular intensity curve $M(q)$ was obtained by dividing the total intensity I_T by the background intensity I_B: $M(q)=(I_T-I_B)/I_B$. Three sets of photographs were taken at the short camera length and two sets at the long camera length and their respective averages were taken. For comparison, a set of photographs of carbon tetrachloride taken in the same condition was analyzed by the same procedure (Section 3 B).

The molecular intensity curves obtained with the long camera length were found to agree with each other to about 0.1 percent. in a relative intensity scale; in addition, it was found possible to connect these curves smoothly with the molecular intensity curves obtained with the short camera length. However, since the molecular intensity for this molecule is small compared with that for carbon tetrachloride (less than 40 percent), considerably larger experimental errors were involved in the photographs taken with the short camera length, particularly in larger scattering angles. Although it is difficult to estimate various sources of experimental errors individually, a rough measure of their total limit may be given by the discrepancy among the three molecular intensity curves shown in Fig. 1.

The corrections for such effects as the beam size, the sample size, and double scattering were not taken into account, because they have little effect on the determination of bond distances,

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9) I. L. Karle and J. Karle, *J. Chem. Phys.*, **20**, 63 (1952).

10) H. J. M. Bowen, A. Gilchrist and L. E. Sutton (*Trans. Faraday Soc.*, **51**, 1341 (1955)) reported the C-Cl bond distance in $CH_2{=}CH\text{-}CH_2Cl$ to be $1.82_5\pm0.025$Å.

11) P. W. Allen and L. E. Sutton (*Trans. Faraday Soc.*, **47**, 236 (1951)) also reported the C-Cl bond distance in CH_3COCl to be 1.82±0.02Å. Note, however, that their conclusion was based on the data extended to a rather small scattering angle, and by our recent reinvestigation, it was found to be 1.77±0.02Å. (Y. Morino, et al., *J. Chem. Soc. Japan*, **75**, 647 (1954)).

12) See for example S. H. Bauer and P. Andersen, *Ann. Rev. Phys. Chem.*, **4**, 233 (1953).

13) G. Herzberg and B. P. Stoicheff, *Nature*, **175**, 79 (1955).

14) Recent X-ray study on solid dimethylacethylene $H_3C\text{-}C{\equiv}C\text{-}CH_3$ has given the following result: C≡C= 1.21_1Å and C-C=1.45_7Å. (E. Pignataro and B. Post, *Acta Cryst.*, **8**, 672 (1955)).

15) K. Kuchitsu, This Bulletin, **30**, 399 (1957).

16) Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, (to be published).

17) Y. Morino, M. Kimura and M. Iwasaki, The Sixth Annual Meeting of the Chemical Society of Japan, April 1953.

18) T. Ino, *J. Phys. Soc. Japan*, **8**, 92 (1953).

19) A. W. Johnson, *J. Chem. Soc.*, **1946**, 1009.

20) The shape of this nozzle is similar to that described by M. Kimura and M. Aoki, This Bulletin, **26**, 429 (1953),

21) J. Karle and I. L. Karle, *J. Chem. Phys.*, **18**, 957, 963 (1950).

22) The microphotometric procedure was carried out by using an apparatus at Nagoya University, collaborated by Mr. H. Morimoto and Mr. S. Shibata.

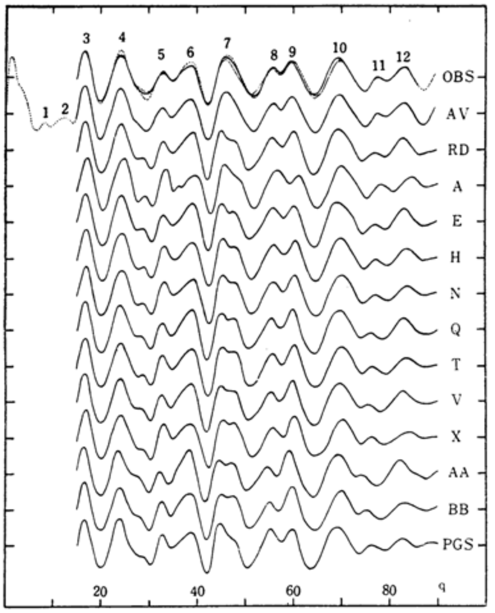

Fig. 1. Observed and calculated molecular scattering intensity curves $qM(q)$ for 1,4-dichlorobutyne.
OBS: three observed intensity curves obtained from independent experiments; AV: the averaged intensity curve, supplemented by a reasonable theoretical intensity curve in the inner region (the dotted curve). The other curves are calculated on the basis of the models indicated in the parameter chart (Fig. 5) (except the models RD and PGS, whose parameters are given in the text).

although they are quite important in the precise investigation of the mean square amplitudes[21,23].

3. Analysis

A. Procedure.—The modified radial distribution (RD) curves[24] were calculated from the molecular intensity curve according to the equation[25]

$$f(r)=\sum_{q=1}^{90} qM(q)\exp(-aq^2)\sin(\pi qr/10), \quad (1)$$

where $M(q)$ is the molecular scattering intensity, the value of a (0.000284) is chosen to make the integrand of Eq. (1) converge rapidly, and $q=(40/\lambda)\sin(\theta/2)$, where θ is the angle of scattering and λ is the wavelength of the electron beam.

The theoretical intensity curves were calculated using the equation[25,26]

$$qM_c(q)=\sum_{i>j}(c_{ij}/r_{ij})\exp(-b_{ij}q^2) \times\sin(\pi qr_{ij}/10), \quad (2)$$

where r_{ij} denotes the interatomic distance between the i-th and the j-th atoms, b_{ij} its temperature factor, and

$$c_{ij}=2Z_iZ_j/\{\textstyle\sum_i Z_i(Z_i+1)\}, \quad (3)$$

except in the analysis of the small angle region[15], where

$$c_{ij}=2(Z_i-f_i)(Z_j-f_j)/\{\textstyle\sum_i(Z_i-f_i)^2+S_i\}, \quad (4)$$

was used[27]; Z_i is the atomic number (for hydrogen, an effective value 1.25 was used in place of unity), and f_i and S_i are the elastic and inelastic atomic scattering factors, respectively[28]. These summations were performed by use of punched cards and a Remington Rand Type-285 Model-2 tabulating machine[29,25].

B. Carbon Tetrachloride.—The photographs of carbon tetrachloride were analyzed in the first place, because this molecule has been frequently used as a reference molecule for the determination of atomic distances. A theoretical intensity curve was computed based on the assumption that the C—Cl distance was 1.766Å, and that the mean amplitudes[30] of the C—Cl and the Cl—Cl distance were 0.054 Å and 0.069 Å, respectively[31]. A comparison of this curve with the observed molecular intensity curve shows a good agreement as illustrated in Fig. 2. The average $q_{\text{calcd.}}/q_{\text{obs.}}$ ratio for twenty-one maxima and minima is 1.000 ± 0.002, and the average fluctuation in the $I_{\text{obs.}}/I_{\text{calcd.}}$ ratio for these maxima and minima is 5.8 percent.

The C—Cl distance obtained from this analysis, $1.76_6\pm0.01$Å, coincides with the

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23) R. B. Harvey, F. A. Keidel and S. H. Bauer, *J. Appl. Phys.*, **21**, 860 (1950).

24) Y. Morino and E. Hirota, *J. Chem. Phys.*, (to be published).

25) P. A. Shaffer, Jr., V. Schomaker and L. Pauling, *J. Chem. Phys.*, **14**, 648, 659 (1946).

26) M. E. Jones and V. Schomaker, *J. Chem. Phys.*, **19**, 511 (1951).

27) The use of Eq. (3) instead of Eq. (4) causes only a small decrease (about 11 percent at $q=17$, 4 percent at $q=20$, and less than 3 percent at $q>25$) in the peak intensity of a theoretical intensity curve.

28) The f_i and S_i values used here were taken from the table in the following textbook: A. H. Compton and S. K. Allison, "X-Rays in Theory and Experiment", 2nd. Ed., D. Van Nostrand Co., New York, (1936) p. 780. These f_i values are essentially the same as the data published recently; for example, H. Viervoll and O. Ögrim, *Acta Cryst.*, **2**, 277 (1949).

29) Y. Morino and K. Kuchitsu *X-Rays*, **8**, 37 (1954).

30) For simplicity, the term "root mean-square amplitude" will be hereafter referred to as "mean amplitude".

31) Y. Morino et al., *J. Chem. Phys.*, **21**, 1927 (1953).

TABLE I

THE RESULT OF THE ANALYSIS OF THE RADIAL DISTRIBUTION CURVE[a)]

		C_1-Cl	C_2-Cl	C_3-Cl	C_4-Cl	$Cl-H$	$Cl-C_2$	$Cl-C_3$
Distance	obs.	1.79_5	2.69	3.71_5	5.08_5	2.38	1.47_7	2.69
	calcd.[b)]	—	2.69	3.71	5.07	2.39	—	2.69
Mean Amplitude	obs.	0.055	0.077	0.080	0.123	0.086	0.054	0.051_a
	estd.[c)]	0.054	0.073	0.080	0.090	0.114	0.047	0.051
Peak Area	obs.	197.9	223.3	171.2	219.7	53.8	67.8	77.6
	calcd.	204.0	204.0	204.0	204.0	85.0	72.0	72.0

		$C\equiv C$	C_1-C_4	C_1-H	C_2-H	C_3-H	C_4-H	$H-H$
Distance	obs.	1.21_3	4.07	1.10_a	2.10	3.18	4.63	1.80_a
	calcd.	—	4.17	—	2.11	3.23	4.65	1.80
Mean Amplitude	obs.	0.061	0.092	0.077_a	0.092	—	0.092	0.120_a
	estd.	0.036	0.060	0.077	0.120	0.120	0.120	0.120
Peak Area	obs.	39.2	63.1	28.3	34.7	17.7	42.8	3.0_a
	calcd.	36.0	36.0	30.0	30.0	30.0	30.0	3.1

a) Equilibrium distances and mean amplitudes are in Å unit. The subscript a denotes that the values listed were assumed in this analysis.

b) The calculated equilibrium distances are based on the four directly-bonded distances obtained from this analysis and the C-C-Cl angle of 110.5°.

c) Estimated values (see Ref. 34).

TABLE II

COMPARISON OF EXPERIMENTAL AND THEORETICAL INTENSITY CURVES[a)]

Peak		Peak Position			Peak Height		
Max.	Min.	q_o	q_c	q_c/q_o	I_o	I_c	I_o/I_c
	1	6.7	6.7	1.000	−0.696	−0.829	0.840
1		8.3	8.3	1.000	−0.440	−0.524	0.840
	2	10.0	10.0	1.000	−0.687	−0.860	0.799
2		12.4	12.4	1.000	−0.367	−0.360	1.019
	3	14.0	13.9	0.993	−0.495	−0.671	0.738
3		16.7	16.7	1.000	1.140	1.393	0.818
	4	19.9	20.1	1.010	−1.018	−1.083	0.940
4		24.2	24.2	1.000	1.038	1.262	0.823
	5	29.7	30.4	(1.023)	−0.698	−0.924	0.755
5		33.0	33.0	1.000	0.222	0.405	0.548
	6	34.8	34.8	1.000	−0.140	−0.162	0.864
6		38.8	38.9	1.003	0.559	0.877	0.637
	7	42.3	42.1	0.995	−1.061	−1.470	0.722
7		45.9	45.2	(0.985)	0.780	0.952	0.819
	8	51.7	50.8	0.983	−0.720	−1.000	0.720
8		55.7	55.6	0.998	0.418	0.619	0.675
	9	57.4	57.7	1.005	0.150	0.143	(1.049)
9		59.6	60.0	1.007	0.682	0.914	0.746
	10	64.5	64.3	0.997	−0.761	−1.238	0.615
10		69.6	69.4	0.997	0.761	0.986	0.772
	11	75.0	74.4	(0.992)	−0.525	−0.545	(0.963)
11		77.3	76.7	(0.992)	0.016	−0.167	(—)
	12	79.1	79.0	(0.999)	−0.160	−0.360	(0.444)
12		82.9	82.8	0.999	0.422	0.600	0.703
	13	86.8	86.4	(0.997)	−0.482	−0.240	(2.008)
Average[b)]				1.000			0.744
Average Deviation				0.004			0.078

a) The theoretical intensity curve is based on the results of the RD analysis. The observed data listed above the line (min. 1∼3) are the data obtained from the long camera-length photographs, and their ratios are not included in the average.

b) The ratios enclosed in parentheses are not included in the average either (see Ref. 42).

TABLE III

DISTANCES OBTAINED FROM $q_{\text{calcd.}}/q_{\text{obs.}}$ VALUES[a)]

Acceptable Models	Average $q_{\text{calcd.}}/q_{\text{obs.}}$	Average deviation	∠C-C-Cl	C−Cl	C−C	C≡C	C−H
J	1.006	0.006	110°	1.80_0	1.47_8	1.21_7	1.10_6
K	1.003	0.005	110°	1.79_6	1.48_5	1.21_4	1.10_5
O	1.004	0.004	111°	1.79_8	1.46_6	1.21_5	1.10_5
P	1.003	0.005	111°	1.79_6	1.47_5	1.21_4	1.10_3
T	1.004	0.005	112°	1.79_6	1.45_5	1.21_4	1.10_4
U	1.001	0.004	112°	1.79_2	1.46_1	1.21_1	1.10_1
Most probable value			111°	1.79_6	1.47_0	1.21_4	1.10_4

a) The distances are in Å unit.

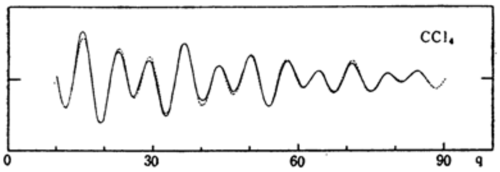

Fig. 2. Molecular intensity curves $qM(q)$ for carbon tetrachloride.
The solid and the dotted curves denote the observed and the calculated intensity curves in a relative scale, respectively.

similar sector-microphotometer data obtained by Karle and Karle[32)] (1.770±0.01Å) and by Bartell and Brockway[33)] (1.766 ±0.003Å).

C. Radial Distribution Curve.—In the calculation of the RD curve by Eq. (1) a molecular scattering curve which was computed from an assumed model (structural parameters and internal rotation) was attached to the experimental curve in the region $q=0\sim15$. A few steps of successive approximations were made in order to get a reasonable background-line which would satisfy Karle's criteria[21)] as closely as possible ($q>15$), and also to make the assumed structural parameters self-consistent with the final RD curve.

In the above calculation various possible conditions of internal rotation were assumed; for instance, free rotation, a cosine-type barrier of 1 kcal./mole, and the rigid trans configuration. The RD curves show considerable difference between each other in the region $r>4.5$ Å, as shown in Fig. 3, particularly in the region of the H⋯Cl and Cl⋯Cl bond distances (5.4–6.4Å), which are dependent on the internal rotation. Therefore we cannot arrive at any confirmative conclusion about internal rotation from this RD curve alone. In order to investigate the internal rotation, it is necessary to examine the experimental molecular scattering curve in the region $q\lesssim15$.

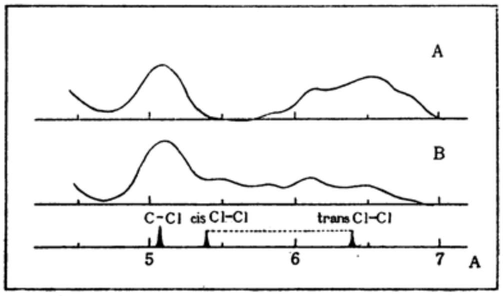

Fig. 3. A portion of a typical radial distribution curve.
(A) Rigid trans model, and (B) free rotation were assumed in the calculation of the theoretical intensity curves ($q=0-15$) which were attached to the same experimental curve. The distances under the curves indicate their approximate positions.

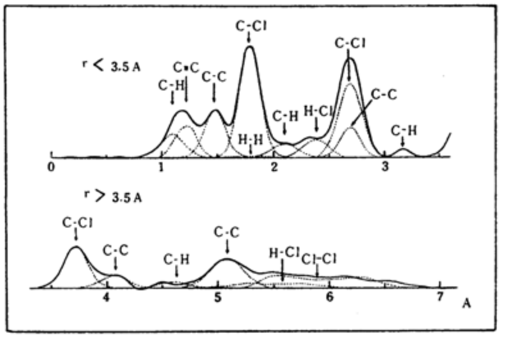

Fig. 4. A typical radial distribution curve for 1,4-dichloro-2-butyne (the solid line). Free internal rotation was assumed. The dotted line indicates the individual peak for each interatomic distance.

On the other hand, these RD curves are found to be quite identical in the region

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32) I. L. Karle and J. Karle, *J. Chem. Phys.*, **17**, 1052 (1949).

33) L. S. Bartell and L. O. Brockway, ibid., **23**, 1854 (1955).

$r \lesssim 4.5$ Å; therefore, by analyzing this region, structural parameters including the mean amplitudes of vibration can be determined without any knowledge of internal rotation. The RD curve, based on the assumption of free rotation, was analyzed in detail as follows. (Fig. 4).

The first peak of the RD curve ($r \lesssim 2.0$Å) was decomposed from the right-hand side successively into the contributions from the C—Cl and C—C distances, leaving a composite peak including the C≡C and C—H distances. To obtain the C≡C distance, the equilibrium distance and the mean amplitude of the C—H bond were assumed to be 1.10 Å and 0.077 Å[34], respectively, since these distances are close together, and it is difficult to separate them unambiguously.

In order to decompose the second large peak ($r \sim 2.7$ Å) into those of the Cl—C_3 and C_2—Cl distances, the sum of the C_1—C_2 and C≡C distances which had been obtained from the analysis of the first peak was used for the C_1—C_3 distance, and 0.051 Å was assumed for its mean amplitude[34].

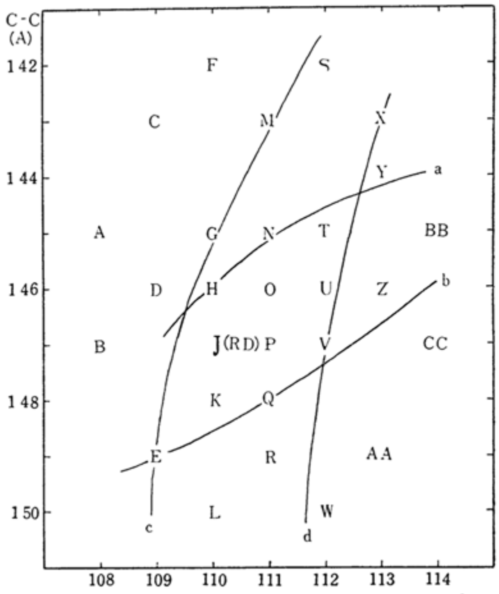
The third peak ($r \sim 3.7$ Å) is due to the C_3—C_1 distance overlapped by the contribution of the C_1—C_4 distance on the right-hand side, and the fourth peak is due to the C_4—Cl distance. These peaks and other smaller peaks were analyzed in the same manner.

The area under the peak multiplied by the equilibrium distance should be proportional to the corresponding c_{ij} value[21]. The areas obtained from the above analysis are in fairly good agreement with the expected values, yet there is a discrepancy of ±15 percent., which indicates that a small amount of "ghost" included in the RD curve changes the shapes of small peaks (particularly in the region $r > 3.5$Å). The most part of this ghost is probably due to the errors in the observed intensity curve. Hence, in order to estimate the uncertainty, RD curves were calculated and analyzed from various experimental intensity curves which differ within the limits of experimental error. In spite of the slight difference in the areas (about 3% for C—Cl peaks, and 10% for C—C peaks) and in the mean amplitudes (about 10% for larger peaks) among various RD curves, the centers of the larger peaks remain practically constant. The possible range of the positions of these main peaks are as follows:

C≡C: 1.20–1.22 Å; C—C: 1.46–1.48 Å;
C—Cl: 1.79–1.80 Å; Cl—H: 2.36–2.38 Å;
C_1—C_3: 2.67–2.70 Å; C_2–Cl: 2.68–2.70 Å;
C_3—Cl: 3.70–3.74 Å.

A typical result of the RD analysis is given in Table I. The distances listed on the second row are calculated from the model with the directly bonded distances listed in the same table, a C–C–Cl angle of 110.5°, and C–C–H and H–C–H angles of 109.5°. The mean amplitudes listed on the third row are the values directly obtained from the Gaussian-type RD peaks, without the correction for second-order effects[21,22], such as a sample size, double scattering, and the failure of Born approximation[35,36].

D. Theoretical Intensity Curves. — A theoretical intensity curve was computed using the values obtained from the RD curve (C—H 1.10 Å, C≡C 1.21 Å, C—C 1.475 Å, C—Cl 1.795 Å, and ∠C–C–Cl



C—Cl=1.79 Å (C≡C=1.21 Å, C—H=1.10 Å, ∠C-C-H=∠H-C-H=109.5)

Fig. 5. Parameter chart for 1,4-dichloro-2-butyne.
The positions of the letters indicate the parameters of the models for which intensity curves in Fig. 1 were computed (except RD, which does not exactly correspond to the parameters of the model RD). The lines a, b, c and d indicate the border-line of the acceptable region for certain particular features.

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[34] The mean amplitudes listed in the fourth row of Table I are either calculated approximately using the force constants of dimethylacetylene (B. L. Crawford, Jr., *J. Chem. Phys.*, **7**, 555 (1939)), or estimated from the Table V and VI of the Reference 31.

110.5°); these values roughly correspond to the point "RD" in Fig. 5. The $q_{\mathrm{calcd.}}/q_{\mathrm{obs.}}$ ratio for the maxima and minima is 1.000 ±0.004 (Table II),[37] and the average fluctuation in the $I_{\mathrm{obs.}}/I_{\mathrm{calcd.}}$ ratio for these maxima and minima is about 10 percent.

In order to determine the range of uncertainty in various parameters, a number of intensity curves were computed based on assumed models. Since it is not feasible to exhaust the seven independent structural parameters and the mean amplitudes, the C≡C and C–H bond distances[38] and the C–C–H and H–C–H angles[39] were kept constant at 1.21 Å, 1.10 Å, and 109.5°, respectively, only the ratio C–C/C–Cl and the angle C–C–Cl being varied systematically. The parameter chart is given in Fig. 5. Estimated mean amplitudes[34] given in Table I were used throughout. Free internal rotation was assumed, and the theoretical intensity curves computed at each rotational angle at 10° intervals were summed up; mean amplitudes of the H–Cl and Cl–Cl distances were assumed to be 0.120 Å and 0.080 Å, respectively at all rotational angles, and the contribution from the H–H distances was ignored. When a high potential barrier is assumed, the resulting intensity curve shows features which completely disagree with the observed curve even in the region $q>15$ so that such a model is definitely excluded. This disagreement is most prominent in the extreme case that the barrier is infinite (i.e., any one of *trans*-, *gauche*- and *cis*-form, similar in configuration to those of 1,2-dichloroethane[40], or one of their possible mixtures). However, when a sufficiently low barrier ($V\leqq 1$ kcal./mole) is assumed, the variation in the barrier from zero causes little change in the features of the theoretical intensity curve, which are thus in fairly good agreement with the observed curve. As a result, the assumption of free internal rotation, in accordance with the result of the following paper[15], may be reasonable in determining the structural parameter limit.

Some of the computed curves are reproduced in Fig. 1. The computed curves have the following features which are sensitive to small changes in some parameters[41]: the relative height of maxima 5 and 6, and that of maxima 8 and 9. The curves in the parameter chart illustrated in Fig. 5 denote the limit where a particular qualitative feature in the computed curves becomes sufficiently different from the experimental curve to be considered unacceptable.

No model above the line a (A, B, C, D, F, G, M, S and X) is acceptable because the fifth maximum is higher than, or almost the same height as the sixth maximum; model H, N and Y are estimated to be on the borderline. Each model below the line b (L, R, W, AA and CC) has too high and sharp sixth maximum, E and Q being estimated to be on the borderline. The line c excludes the models A, B, C, D and F because the eighth maximum has too high and broad features in each of them. The line d excludes the models Y, Z, AA, BB and CC because the ninth maximum is too high. Acceptable models, which are in the region enclosed

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35) Recently, J. A. Ibers and J. A. Hoerni (*Acta Cryst.*, **7**, 405 (1954)) calculated a scattering phase shift η, in the form applicable to any atom under any voltage not too different from 40 KeV. The percentage apparent increase in the mean amplitudes of C-Cl, H-Cl and C-H distances due to this effect was calculated by use of their tables to be about 10%, 7% and 1%, respectively, the first one being in exact agreement with the corresponding value estimated be Bartell and Brockway (Ref. 36b)).

36), a) R. Glauber and V. Schomaker, *Phys. Rev.*, **89**, 667 (1953).

b) L. S. Bartell and L. O. Brockway, *Nature*. **171**, 978 (1953).

37) The ratios for some maxima and minima are not included in the average. See Ref. 42.

38) The C≡C bond distance was found to be 1.207 Å is methylacetylene (L. F. Thomas, E. I. Sheppard and J. Sheridan, *Trans. Faraday Soc.*, **51**, 619 (1955)), and as pointed out by Herzberg and Stoicheff (Ref.13) and many other authors, C≡C bond distance remains remarkably constant in various molecules independent of the atoms linked to this system through a single bond. The result of the above RD analysis is also consistent with this fact. Thus, it will be reasonable in this case to fix the C≡C bond distance at 1.21Å. See also Ref. 12

39) Recent measurement of line shapes of nuclear magnetic resonace absorption led to an H-H distance of 1.71±0.02Å in the CH_2Cl-group of 1,2-dichloroethane (H. S. Gutowsky, et al., *J. Chem. Phys.*, **17**, 972 (1949)). These authors pointed out that the H-C-H angle of this group is significantly smaller than the tetrahedral angle if the C-H distance of 1.10Å or 1.09Å is assumed. Since no corresponding data have yet been found in 1,4-dichlorobutyne, and since the contributions of hydrogen terms to the total intensity curve are relatively small, tetrahedral angles were assumed for both H-C-H and C-C-H angles throughout this investigation.

40) S. Mizushima, "Structure of Molecules and Internal Rotation", Academic Press Inc., New York, (1954), p. 8.

41) Although the drawing of the background line is not unique, the relative heights of adjacent maxima are little changed by the redrawing of the background line, only if the line is smooth and roughly fulfills karle's criteria. As illustrated in Fig. 1, absolute heights of the maxima 5, 6, 8 and 9 change among the measurements of different photographs; nevertheless, the relative ratios of the peaks 5 to 6, and 8 to 9 remain nearly constant. For this reason, these ratios are regarded as the essential features of the experimental intensity and are used as the criteria for the following analysis.

by these four lines, are J, K, O, P, T and U[42].

The area of this "acceptable region" cannot be further reduced by taking other features into account such as the relative depths of minima, because small differences in these features are not significant enough to exclude any of these acceptable models.

The average $q_{\text{calcd.}}/q_{\text{obs.}}$ values for these acceptable models and the C—Cl and C—C distances determined from these averages are listed in Table III; they all agree satisfactorily with the RD results. The final choice of parameters with their estimated limits of uncertainty (including the error in the determination of q scale, which is estimated to be less than 0.4 percent) are as follows:

C—Cl: $1.79_6 \pm 0.01_5$ Å,
C≡C: 1.21_4 Å (not varied),
C—C: $1.47_0 \pm 0.02_5$ Å,
(C—H: 1.10_4 Å, assumed),
∠C–C–Cl: 111°±2°
(∠C–C–H = ∠H–C–H: 109.5°, assumed).

The C—Cl distance in this molecule is somewhat shorter than that of propargyl chloride (1.82±0.02 Å) found by Pauling et al.[7]. The theoretical intensity curve, based on the model in which all parameters were set equal to the values of propargyl chloride determined by these authors (C—Cl: 1.82 Å, C—C: 1.48 Å, C≡C: 1.20 Å, and ∠C–C–Cl: 111°), is shown as the curve PGS in Fig. 1. It shows a qualitative difficulty in the maximum 8, and its $q_{\text{calcd.}}/q_{\text{obs.}}$ average is less than unity (0.994±0.006).

4. Discussion

The C≡C and C—C distances obtained above agree, within the limit of experimental uncertainty, with those of similar molecules studied both by spectroscopy and by electron and X-ray diffraction[12–14]. It is a remarkable fact that the C—C distances in various molecules (1.46–1.47 Å) are much shorter than the normal C—C single-bond distance (ca. 1.54 Å), and that they are almost independent of the atoms or groups linked to the carbon atoms.

The C–C–Cl angle (111°±2°) is nearly the same as that in 1,2-dichloroethane (110°23′)[43] and in ethyl chloride (110°30′)[44], while the C—Cl distance ($1.79_6 \pm 0.01_5$ Å) seems to be a little longer than that in the latter molecules (1.78±0.01 Å, and 1.7770 Å, respectively). The increase in the C—Cl bond distance in this molecule compared with that in carbon tetrachloride ($1.76_6 \pm 0.01$ Å) will be real, because these data were obtained at the same condition and by the same procedure. The lengthening of the C—Cl bond is still more pronounced in propargyl chloride which was investigated by Pauling and his coworkers (1.82±0.02 Å)[7], but it is not yet clear whether there is any actual difference between the C-Cl bonds in 1,4-dichloro-2-butyne and in propargyl chloride.

Pauling and his coworkers attributed the lengthening of the C—X bond in propargyl halides to the contribution of the resonance structure (II):

$$\text{(I)}\quad \mathrm{H{-}C{\equiv}C{-}CH_2{-}X},$$

$$\text{(II)}\quad \mathrm{H{-}\overset{+}{C}{=}C{=}CH_2\quad X^-}.$$

If this were actually the case, large contribution of the similar resonance structures (III) and (IV):

$$\text{(III)}\quad \mathrm{Cl{-}H_2C{-}\overset{+}{C}{=}C{=}CH_2Cl^-},$$

$$\text{(IV)}\quad \mathrm{Cl^-\ H_2C{=}C{=}\overset{+}{C}{-}CH_2Cl},$$

would also be expected in 1,4-dichloro-2-butyne, whereas a recent measurement[45] of the dipole moments of propargyl chloride, bromide, and 1,4-dichloro-2-butyne has shown that these molecules have

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[42] These acceptable curves still have a slight disagreement with the experimental curve: namely, (a) the existence of the shoulders of minimum 5 and maximum 7, and (b) the feature near maximum 11. The discrepancy (b) cannot be taken so seriously because precise measurement of this region could not be made in this experiment. The discrepancy (a), however, should be noted, because it is not clear whether the main origin is in the experimental error or in the assumption of the computation.

Although the structural parameters of the acceptable models are consistent with the RD results, and the assumptions of temperature factors and of free internal rotation seems to be reasonable as stated above. there still remains some possibility that we may find a more satisfactory model by changing some of the parameters.

If, on the other hand, this discrepancy comes from the error in the experimental procedure, in other words, if these shoulders do exist, and were not resolved in this experiment, it corresponds to an error of the order of the width of the microphotometer trace (ca. 0.2 mm.). Although this is apparently larger than that of our usual measurement, existence of comparable error in these regions is suggested by the fact that the largest discrepancies among the three observed curves are found in these regions (Fig. 1). On the visual interpretation of the original diffraction pattern, no such shoulders can be clearly observed; but, of course, this visual estimation should not be conclusive.

For this reason, the $q_{\text{calcd.}}/q_{\text{obs.}}$, values of max. 7, 11, and min. 5, 11, 12 and 13 are not included in calculating their averages and average deviations.

[43] J. Ainsworth and J. Karle, *J. Chem. Phys.*, **20**, 425 (1952).

[44] R. S. Wagner and B. P. Dailey, ibid., **25**, 1355 (1955).

[45] T. Chiba, T. Simozawa, I. Miyagawa and Y. Morino. This Bulletin, **30**, 223 (1957).

smaller C—X bond dipole moments than the normal C—X bond moments, in apparent contradiction to the above expectation. Consequently, it seems difficult to explain the lengthening of the C—Cl bond on the basis of these resonance structures.

Summary

The structure of 1, 4-dichloro-2-butyne was investigated by means of the sector-microphotometer method of electron diffraction. The following values were obtained: C≡C: 1.21_4 Å, C—C: $1.47_0 \pm 0.02_5$ Å, C—Cl: $1.79_6 \pm 0.01_5$ Å, and ∠C-C-Cl: 111° ±2°. The C—Cl distance was found to be longer than that in carbon tetrachloride, $1.76_6 \pm 0.01$ Å.

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