changes is again illustrated. It has been indicated recently that when collagen is tanned with an epoxy resin, reversible dimensional changes also are observed.[58]

On the basis of the above discussion, it can be deduced that anisotropic dimensional changes in the fibrous proteins can be attributed to a phase transformation between the crystalline and amorphous states, and in analogy with fibrous polyethylene for oriented recrystallization to occur without the application of any external force, intermolecular cross-links must be imposed on the system when the chains are in an oriented state. It may be expected that with further investigations the contractile processes observed in other naturally occurring fibrous macromolecular systems may receive explanation from similar considerations. In fact, it has been proposed by Pryor[40] and by Flory[2,4] that the contraction of muscle is caused by the melting or the partial melting of the highly ordered polypeptide chains comprising the myofibril. The validity of applying these principles to the muscle system must, of course, await further experimental confirmation.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

The Molecular Structure of 1,1-Dichloroethane by Electron Diffraction[1]

BY M. D. DANFORD AND R. L. LIVINGSTON

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The molecular structure of 1,1-dichloroethane has been investigated by electron diffraction using the visual correlation procedure, with qualitative aid by the sector method. The following results were obtained: C–Cl = 1.795 ± 0.02 Å., Cl--Cl = 2.925 ± 0.03 Å., C–C = 1.55 ± 0.07 Å., and ∠C–C–Cl = 110 ± 4°. Results are compared with those obtained for other chloroalkanes.

Introduction

Structural investigations of most chloroalkanes have yielded C–C distances ranging from 1.54 to 1.56 Å. However, an electron diffraction investigation of the structure of 1,2-dichloroethane by Ainsworth and Karle,[2] using the rotating sector method, yielded an unusually short C–C distance of 1.49 ± 0.03 Å. In addition, an X-ray diffraction investigation of the crystal structure of solid 1,2-dichloroethane by Reed and Lipscomb[3] gave C–C = 1.49 ± 0.04 Å. The present investigation was undertaken to attempt to determine whether any difference exists between the C–C bond distances in 1,1-dichloroethane and in 1,2-dichloroethane and to compare the C–Cl distance in 1,1-dichloroethane with similar distances in other chloroalkanes.

Experimental

The 1,1-dichloroethane was obtained from a commercial sample and subjected to numerous distillations, with the middle portion of the final fraction, boiling at 57.2° (uncorrected), being used for preparation of photographs. Photographs which extended to $q = 90$ were obtained for visual analysis, and four plates with electron wave lengths ranging from 0.05495 to 0.05933 Å. were selected for analysis. Sector photographs extending from $q = 21$ to $q = 52$ were taken to aid in the determination of feature intensities in this range, and two plates, both with electron wave lengths of 0.05527 Å., were traced with a Leeds and Northrup recording microphotometer. The visual curve is the result of about twenty-five measurements of one author (M.D.) and intensity assignments for each feature by both authors. Both the visual and sector curves are shown in Fig. 1.

The radial distribution[4,5] and visual correlation method[6,7] were used in the analysis of the diffraction pattern. Theoretical intensity curves were calculated by the equation

$$I(q) = \sum_i \sum_j \frac{Z_i Z_j}{r_{ij}} \exp(-b_{ij}q^2) \sin \frac{\pi q r_{ij}}{10} \qquad (1)$$

using punched cards.[5] The constant b_{ij} in the vibration factor was assigned the values 0.00016 for bonded C–H terms, 0.0003 for non-bonded C---H and Cl---H terms, 0.00008 for non-bonded C---Cl terms and zero for the other terms.

TABLE I

QUANTITATIVE ELECTRON DIFFRACTION DATA FOR 1,1-DICHLOROETHANE

Max.	Min.	q_{obsd}	E_3 q/q_0	D_3 q/q_0	C_5 q/q_0	B_4 $q,/q_0$
1		16.37	(0.947)	(0.947)	(0.947)	(0.947)
	2	19.80	(0.979)	(0.980)	(0.981)	(0.981)
2		23.06	1.006	1.008	1.010	1.012
	3	26.30	1.005	1.005	1.006	1.007
3		29.01	1.002	0.999	0.996	0.993
	4	33.00	0.986	0.986	0.986	0.985
4		36.60	0.998	0.999	1.000	0.998
	5	40.56	(0.999)	(0.999)	(1.000)	(1.002)
5		43.64	(1.019)	(1.017)	(1.016)	(1.016)
	6	46.02	(1.010)	(1.010)	(1.009)	(1.007)
6		48.25	(1.009)	(1.013)	(1.018)	(1.021)
	7	52.99	0.999	0.999	1.001	1.004
7		56.31	1.020	1.019	1.019	1.020
	8	65.92	0.993	0.992	0.993	0.994
8		69.47	1.004	1.002	1.002	1.002
	9	73.22	(1.010)	(1.007)	(1.006)	(1.006)
9		76.28	(1.015)	(1.016)	(1.016)	(1.015)
	10	79.28	(0.993)	(0.993)	(0.996)	(0.998)
10		82.25	1.006	1.005	1.004	1.005
	11	86.70	1.002	1.001	1.000	1.000
11		89.93	1.010	1.012	1.012	1.010
	Av.		1.003	1.002	1.002	1.003
	Av. dev.		0.006	0.006	0.006	0.007

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(1) Contains material from the Ph.D. thesis of M. D. Danford, Purdue Research Fellow in Chemistry, 1953–1954.

(2) J. Ainsworth and J. Karle, *J. Chem. Phys.*, **20**, 425 (1952).

(3) T. B. Reed and W. N. Lipscomb, *Acta Cryst.*, **6**, 45 (1953).

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

(5) L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935).

(6) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

(7) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

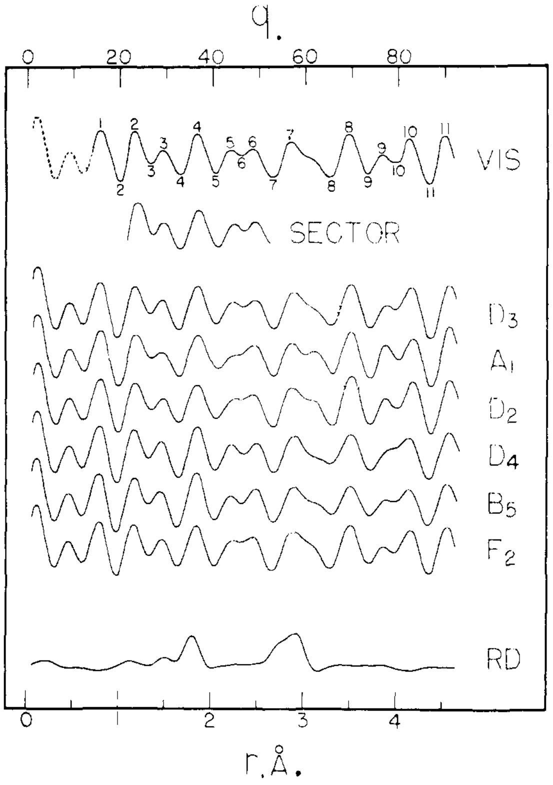

Fig. 1.—Observed intensity curves, calculated intensity curves and radial distribution curves for 1,1-dichloroethane.

Staggered models of symmetry C_s were assumed and the scale of all models was fixed by setting C–Cl = 1.79 with the HCC angles and the C–H distances assumed to be 109° 28′ and 109 Å., respectively. The C–C distance and ∠C–C–Cl were varied in planes with fixed Cl–C–Cl angles, as shown by the parameter chart in Fig. 2. Models were surveyed in planes with Cl---Cl 2.88, 2.92 and 2.96 A., with acceptable models being found only in the Cl---Cl 2.92 Å. plane, as indicated by the dotted line in Fig. 2 which encloses the range of acceptability. Curve D_3 in Fig. 1 represents one of the most acceptable models, while other curves were rejected for several reasons.

Curve A_1 shows maximum 5 as a shoulder rather than as a distinct peak, in addition to the unacceptable shape of the shoulder on the outside of maximum 7. Curves for models B_3 and E_2, indicated on the parameter chart in Fig. 2, were rejected for the same reasons. In curve D_2, maximum 5 is too weak to be acceptable, and similar curves for models C_1 and A_2 also were rejected. Curve D_4 shows only a weak shoulder on the outside of maximum 7, as do curves for models E_1 and F_3, and all of these show a shoulder rather than a peak on the inside of maximum 10. Curves for models C_6 and B_5 have the doublet feature (maximum 5, minimum 6 and maximum 6) too well resolved, with maximum 5 too weak as illustrated by curve B_5 while, in addition, maximum 9 is not sufficiently resolved in curve B_5. The doublet feature in curve F_2 is not well enough resolved to be acceptable. The q/q_0 values for the four acceptable models are listed in Table I, and the final results in Table II. Maxima 1, 5, 6 and 9 and minima 2, 5, 6 and 10 were omitted in determining the scale factor because measurements of these features were not considered reliable.

The radial distribution function (Fig. 1) was calculated by the equation

$$rD(r) = \sum_{q\,=\,1,2,3\ldots}^{q_{\max}} I(\text{obsd.})\exp(-bq^2)\sin\frac{\pi q r_{ij}}{10} \qquad (2)$$

where $\exp(-bq^2) = 0.10$ for $q = q_{\max}$. (The inner portion of the curve was obtained from one of the best theoretical curves.) Major peaks were obtained at r values of 1.80 and 2.91 A., representing the C–Cl distance and a combination of the Cl---Cl, C---Cl and minor distances, respectively. The peaks at 1.13 and 1.51 Å. represent the C–H and C–C distances, respectively, but are not considered reliable. The major peaks agree well with the final results listed in Table II.

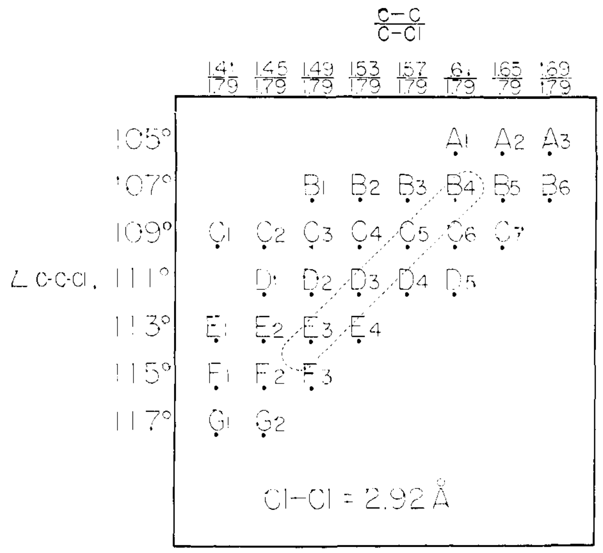

Fig. 2.—Parameter chart for calculated intensity curves for 1,1-dichloroethane.

TABLE II

PARAMETERS OBTAINED FROM ACCEPTABLE MODELS

Parameter	Model E_3	D_3	C_5	B_4	RD[a]
C–Cl	1.795	1.793	1.793	1.795	1.80
Cl---Cl	2.928	2.925	2.925	2.928	2.91
C–C	1.494	1.533	1.573	1.614	1.51
C---Cl	2.748	2.746	2.743	2.743	..
∠C–C–Cl	113°	111°	109°	107°	..

Results of this investigation

C–Cl	$1.79_5 \pm 0.02$ Å.
Cl—Cl	$2.92_5 \pm .03$ Å.
C–C	$1.55 \pm .07$ Å.
C–Cl	$2.74_5 \pm .03$ Å.
∠C–C–Cl	110° ± 4°

[a] RD, radial distribution curve.

Discussion of Results

The value obtained for the C–Cl distance ($1.79_5 \pm 0.02$ Å.) in this investigation is higher than those reported for most other chloroalkanes, with the exception of 1,2-dichloropropane[8] and *t*-butyl chloride,[9,10] where the C–Cl distances are 1.79 and 1.80 Å., respectively. There seems to be no regular trend observable in the C–Cl distance with increasing substitution of chlorine atoms on the same carbon atom, contrary to results obtained for fluorine substituted compounds. One example is the series ethyl chloride,[11] 1,1-dichloroethane, methylchloroform[9] and carbon tetrachloride.[12] A systematic decrease in the C–Cl distance might be expected with increasing substitution of chlorine

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(8) W. W. Wood and V. Schomaker, *J. Chem. Phys.*, **20**, 555 (1952).

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(10) O. Bastiansen and L. Smedvik, *Acta Chem. Scand.*, **7**, 652 (1953).

(11) V. Schomaker, reported by P. W. Allen and L. S. Sutton, *Acta Cryst.*, **3**, 46 (1950).

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

atoms for hydrogen atoms in this series due to a decrease in the ionic character of the chlorine atoms as more chlorine atoms are attached to the same carbon atom. Such a trend is observed for 1,1-dichloroethane, methylchloroform and carbon tetrachloride, the values of the C–Cl distances being 1.795, 1.775 and 1.76 Å., respectively, but an inconsistency occurs in ethyl chloride, where the C–Cl distance is 1.77 Å.

The C–C–Cl and Cl–C–Cl angles (110 ± 4° and 109.5 ± 1.5° respectively) obtained in this investigation are in excellent agreement with results obtained for most of the investigations on other chloroalkanes except *t*-butyl chloride[9,10] and 1,2-dichloropropane,[8] where the C–C–Cl angles are approximately 107 and 108°, respectively. The greatest difference between the results of this investigation and those of other investigations, however, lies in the non-bonded C—Cl distance ($2.74_5 \pm 0.03$ Å.), which is longer than any value reported previously, except for the early value reported by Beach and Stevenson[13] for ethyl chloride (2.74 ± 0.02 Å.).

The large uncertainty on the C–C distance in 1,1-dichloroethane makes it impossible to be certain that this distance is different from the corresponding distance in 1,2-dichloroethane, but it does seem most likely that the latter compound is very unusual in this respect.

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(13) J. Y. Beach and D. P. Stevenson, THIS JOURNAL, **61**, 2643 (1939).

LAFAYETTE, INDIANA

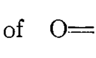
[CONTRIBUTION FROM THE CHEMICAL LABORATORY, TOKYO INSTITUTE OF TECHNOLOGY]

The Molecular Structure of α-Chlorocyclohexanone

BY KUNIO KOZIMA AND YOSHIKO YAMANOUCHI

RECEIVED MARCH 9, 1959

By the measurements of the infrared spectra and the dipole moment of α-chlorocyclohexanone the following results have been obtained that the molecules of α-chlorocyclohexanone in the vapor or the liquid state are in a dynamic equilibrium of mutually convertible isomers represented by the usual symbols as follows (e) ⇄ (a) and that the (e)-form is more stable in the liquid state and only this form persists in the solid state. The energy difference between the isomers was approximately determined. Variation of the energy difference with solvents can be estimated by use of the reaction field theory of Onsager.

It has been well established that the ring structure of various cyclohexane derivatives is the chair form. Because the valency angle of  $O{=}C\langle^{C}_{C}$ of cyclohexanone should be about 120°, its ring structure may be somewhat different from that of usual cylcohexane derivatives. It seems reasonable, however, that the ring structure is nearly the chair form. We can expect, therefore, that the molecules of α-chlorocyclohexanone in the vapor or the liquid state are in a dynamic equilibrium of the two mutually convertible isomers (inverted isomers)[1] represented by the usual symbols[2] as

$$(e) \rightleftarrows (a)$$

where e and a represent the position of chlorine atom attached to the ring, respectively. Both forms are shown schematically in Fig. 1.

In an earlier paper[3] it was described that most of the molecules of α-chlorocyclohexanone in the liquid exist as the axial form, although a small amount of the equatorial form probably exists.

This work was undertaken with the primary purpose of determining the energy difference between the two isomers, special interest being centered in the determination of the more stable form of this compound.

α-Chlorocyclohexanone was prepared by the method of Bartlett and Rosenwald[4] and had b.p. 71.5–72.5° at 6 mm., m.p. 23.0°.

The measurements of infrared absorption spectra were made with a Perkin–Elmer 112 spectrometer. NaCl and KBr prisms were employed to cover 2 to 25 μ. A CaF_2 prism was used to study the band shape of the C=O stretching vibrations.

The Raman spectrograph and other apparatus used in this work have been described previously.[1a]

The wave number readings of the Raman bands and the infrared absorption maxima are listed in Table I. The intensities are shown by the usual symbols, respectively. Carbon disulfide was used for obtaining the spectra in non-polar solvent. Because of the overlap of the absorption of carbon disulfide and that of the solute, the bands at 1438 and 1450 cm.$^{-1}$ for non-polar solvents were obtained in carbon tetrachloride.

In order to determine the energy difference between the two isomers, the temperature dependence of the relative intensities of the two bands at 917 and 933 cm.$^{-1}$ which are due to the different forms of the compound was measured for the CS_2 dilute solution and for the pure liquid. The true integrated absorption intensities *A* corrected for finite slit widths were calculated from the equation

$$A = K(1/CL)\log_e(T_0/T)_{\nu(\max)} \times \Delta\nu^{a}{}_{1/2}$$

where the letters have their usual meanings. The values of *K* were obtained from the table of Ramsay.[5] The results obtained are shown in Table II.

The dipole moment was measured by the usual solution method. The results are shown in Table III.

Discussion of Results

As is clear in Table I, the infrared bands of the liquid spectra are divided into two groups, ac-

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(1) (a) K. Kozima and T. Yoshino, THIS JOURNAL, **75**, 166 (1953); (b) K. Kozima, K. Sakashita and S. Maeda, *ibid.*, **76**, 1965 (1954).

(2) D. H. R. Barton, O. Hassel, K. S. Pitzer and V. Prelog, *Nature*, **172**, 1096 (1953); *Science*, **119**, 49 (1953).

(3) E. J. Corey, THIS JOURNAL, **75**, 2301 (1953).

(4) P. D. Bartlett and R. H. Rosenwald, *ibid.*, **56**, 1992 (1934).

(5) D. A. Ramsay, *ibid.*, **74**, 72 (1952).