Dans quatre cas analysés par cette méthode, le rapport de la valeur moyenne minimum de b à sa valeur maximum a été de 2. Ce qui montre que la valeur quadratique moyenne de l'erreur relative systématique est de l'ordre de 20%.

On peut illustrer le sens de la limite du processus d'affinement en portant en abscisses les ordres successifs des essais au cours de ce processus que nous considérons convergent, et en ordonnées, la valeur du carré du coefficient de corrélation linéaire r (Fig. 1). Le coefficient r^2 tend vers 1 quand l'ordre de l'essai croît, c'est à dire que l'accord entre le calcul et l'observation tend à devenir parfait. Mais pour toutes valeurs de r^2 superieures à $(1-\varepsilon_s^2)$ la précision physique de la structure reste inchangée. Nous sommes limités par la valeur de l'erreur systématique sur l'observation si le nombre d'observations est grand, et par l'erreur totale (systématique et fortuite) si ce nombre n'est pas très grand par rapport à m.

Toute interprétation de la structure faite au delà de cette limite n'a aucune signification physique. Cette interprétation ne pourra que décrire des modifications de la densité électronique qui ne sont dues qu'aux erreurs de mesure.

Remarque I.—Observons que l'erreur ultime ε_U peut s'écrire:

$$\varepsilon_U^2 = \tfrac{1}{2}\Sigma_j(F_{jo}-F_{jc})^2/\Sigma_jF_{jc}^2 \qquad (14')$$

et qu'il a une forme semblable au coefficient R_2 défini par Booth (1945):

$$R_2 = \Sigma_j(F_{jo}-F_{jc})^2/\Sigma_jF_{jo}^2$$

mais la relation (14) ou (14') a une signification physique parce qu'elle est liée à l'erreur experimentale ε_o.

Remarque II.—Le développement ci-dessus donne des arguments importants pour l'adoption du coefficient de corrélation linéaire de Bravais–Pearson r pour l'évaluation de la précision d'une structure en remplacement du facteur de 'reliability' R utilisé par la plupart des cristallographes ($R = \Sigma|F_o-F_c| \div \Sigma|F_o|$).

En effet, seul le coefficient r de Bravais–Pearson a un sens statistique et sa grandeur, comme nous l'avons montré, est liée simplement à l'erreur du modèle proposé d'une structure.

Nous préconisons l'usage du coefficient de correlation linéaire r comme indice de la précision d'une structure.

Nous tenons à remercier tour particulièrement Monsieur le Professeur J. Wyart, ainsi que Messieurs H. Curien, R. Kern et G. von Eller pour l'intêret qu'ils ont apporté à notre travail et par leurs critiques.

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The Crystal Structure of Acetic Acid*

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Acetic acid crystals are orthorhombic, space group $Pna2_1$, with $a = 13{\cdot}32 \pm 0{\cdot}02$, $b = 4{\cdot}08 \pm 0{\cdot}01$, $c = 5{\cdot}77 \pm 0{\cdot}01$ Å from single-crystal X-ray diffraction. The structure is similar to that of formic acid with molecules linked into infinite chains by hydrogen bonds. The bond distances are C–C = 1·54 Å, C=O = 1·24 Å, C–O = 1·29 Å, and O–H · · · O = 2·61 Å, each ±0·02 Å, by least-squares refinement. The four heavy atoms of each molecule lie in a plane. The adhesion between chains is due to van der Waals forces.

Introduction

The structure of acetic acid (CH_3COOH) has been investigated in the gas by electron diffraction by Karle & Brockway (1944) and in solution by infra-red spectroscopy by Davies & Sutherland (1938). The present work was undertaken to give further information on the structure of the molecule and on the forces between molecules in the solid state.

The normal fatty acids are thought to form dimers

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by hydrogen bonding in the gaseous and liquid states. Investigations of members of this series of high molecular weight have shown that dimers are also formed in the solid (Vand, Morley & Lomer, 1951; von Sydow, 1956). However, the lowest member of the series, formic acid, forms infinite hydrogen-bonded chains, rather than dimers, in the solid (Holtzberg, Post & Fankuchen, 1953). Rigaux (1954) has cited spectroscopic evidence that acetic acid also forms polymers rather than dimers in the solid. The results of the present work confirm that the molecules in the crystal are linked together in chains, as in formic acid.

Experimental procedure

Single crystals of acetic acid were prepared by freezing C. P. grade glacial acetic acid (99·8% pure) in a jet of cold nitrogen gas. The liquid was sealed in a glass capillary and quickly frozen into a translucent aggregate of small crystals. The temperature was raised near to the melting point and maintained there for several hours until a transparent single crystal had grown. Its growth was followed by oscillation pictures taken periodically until the small crystallites had vanished.

The flow of cold nitrogen was evolved from liquid nitrogen electrically heated by a resistor in a Dewar flask. The rate of flow was controlled by adjusting the current in the resistor. Since the crystal had to be maintained for many days, two duplicate nitrogen boiling units were made so that one could be taken out of operation and refilled without interrupting the flow for more than a few seconds.

The single-crystal photographs were taken on a Weissenberg camera using Cu $K\alpha$ X-rays. The single crystals showed no tendency to be formed with a crystallographic axis parallel to the capillary axis, so they were aligned using oscillation photographs. The Weissenberg photographs were taken, using a film holder modified so that the upper half was absent to facilitate cooling of the sample. While these photographs were taken the crystal was maintained at $5°\pm5°$ C. The temperature measurements were made using an iron–constantan thermocouple with a reference bath at 0° C.

Unit cell and space group

From oscillation, rotation, and Weissenberg films taken with rotation about the [010] and [011] directions it was deduced that the unit cell was orthorhombic, in agreement with the observations of Steinmetz (1921) on the cleavage and optical properties. The cell dimensions, from Weissenberg photographs calibrated with a quartz crystal, are:

$$a = 13{\cdot}32\pm0{\cdot}02,\quad b = 4{\cdot}08\pm0{\cdot}01,\quad c = 5{\cdot}77\pm0{\cdot}01\ \text{Å}$$
$$(t = 5°\ \text{C.},\ \lambda(\text{Cu}\ K\alpha) = 1{\cdot}5418\ \text{Å})\ .$$

With four molecules per unit cell, the calculated density, 1·27 g.cm.$^{-3}$, agrees with that observed at the melting point by de Visser (1893), 1·26585 g.cm.$^{-3}$.

Reflections were observed for $h0l$ only with $h = 2n$ and for $0kl$ only with $k+l = 2n$. These extinction rules correspond to probable space groups $Pna2_1$ and $Pnam$. A satisfactory structure was found using the space group $Pna2_1$–C_{2v}^9 with atoms in the positions $4(a)$:

$$x, y, z;\ \bar{x}, \bar{y}, \tfrac{1}{2}+z;\ \tfrac{1}{2}-x, \tfrac{1}{2}+y, \tfrac{1}{2}+z;\ \tfrac{1}{2}+x, \tfrac{1}{2}-y, z\ .$$

Intensity corrections

Estimates of the intensities of the reflections on the Weissenberg films were made by visual comparisons with standard spots. The data were corrected for Lorentz and polarization effects. No correction was made for absorption by the sample or the capillary, since this correction was estimated to be small. The corrections were made using an IBM 650 computer. The program, which was prepared with the help of Dr A. Zalkin, also calculated for each reflection the magnitude of the observed structure factor, $\sin^2\theta$, and scattering factors for each kind of atom; determined which formula would be used for calculating the structure factor; and determined the selection of the weight to be used in the program for least-squares refinement. The output cards from this program were used as input cards in the least-squares refinement program.

Determination of the structure

The probable space groups are the same as for formic acid. Therefore, an analogous trial structure was constructed with molecules hydrogen-bonded in chains approximately parallel to the (011) and (01$\bar{1}$) planes. Fourier projections (non-centric) along b with phases based on this structure seemed reasonable, but failed to refine to good agreement with the data for unknown reasons. However, trial-and-error adjustment of the x and z parameters resulted in agreement (R_1 as defined below) of 0·18. With y parameters based on reasonable atomic distances, and some additional trial and error, this structure refined successfully with three-dimensional least squares. The electron density [010]

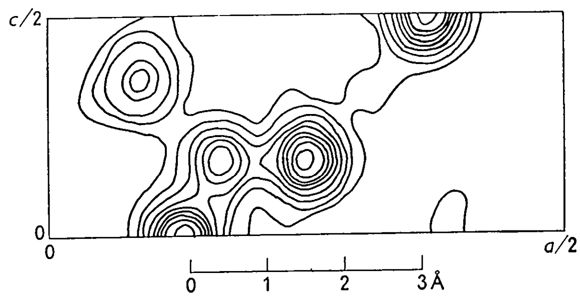

Fig. 1. Electron density of acetic acid projected along [010]. Contours are at intervals of 1 e.Å^{-2}. The zero contour is omitted.

projection based on the final structure is shown in Fig. 1.

The least-squares refinement of the parameters was also done with the IBM 650 computer with a program written largely by Senko (1957). The weights w were taken as the lesser of $(16F^2_{\text{min.}})^{-1}$ or $(F^2)^{-1}$, according to Hughes (1941). Three 'unreliability factors' were calculated, using all the data with the observed structure factor, F_o, set equal to zero for unobserved reflections. The results were:

$$R_1 = \Sigma||F_o|-|F_c||\div\Sigma|F_o| = 0{\cdot}158\ ,$$
$$R_2 = (\Sigma||F_o|-|F_c||^2\div\Sigma|F_o|^2)^{\frac{1}{2}} = 0{\cdot}160\ ,$$
$$R_3 = (\Sigma w||F_o|-|F_c||^2\div\Sigma w|F_o|^2)^{\frac{1}{2}} = 0{\cdot}161\ .$$

R_3 is the function actually minimized in the least-squares refinement.

The final coordinates and their standard deviations are listed in Table 1. Also listed are values

Table 1. *Final atomic parameters and isotropic temperature factors*

	x	y	z	B (Å^2)
O_I	0·1295±0·0003	0·103±0·002	0·000±0·001	3·9
O_{II}	0·2526±0·0004	0·369±0·002	0·178±0·001	4·5
C_I	0·1641±0·0006	0·276±0·003	0·170±0·002	3·7
C_{II}	0·0868±0·0006	0·372±0·003	0·357±0·002	4·0

for B in the expression for the temperature factor, $\exp(-B\sin^2\theta/\lambda^2)$. These correspond to root-mean-square vibration amplitudes, $(2B)^{\frac{1}{2}}/4\pi$, from 0·21 to 0·24 Å.

The observed and calculated structure factors are compared in Table 2.

Discussion of the structure

The structure is illustrated in Fig. 2. Molecules are linked together by hydrogen bonds in infinite chains

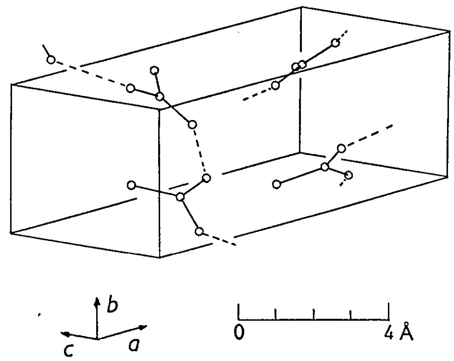

Fig. 2. Crystal structure of acetic acid. Dashed lines represent hydrogen bonds between oxygen atoms. Hydrogen atoms are not shown.

in substantially the same way as in formic acid. Forces between chains are presumed to be van der Waals attractions.

Table 2. *Observed and calculated structure factors*

Structure factors are grouped according to k and l, which are given at the beginning of each sequence. An x in place of $|F_o|$ indicates that the beam catcher blocked the reflection.

h	$\lvert F_o\rvert$	$\lvert F_c\rvert$
	h00	
0	--	280
2	x	79
4	50	45
6	34	33
8	46	42
10	24	22
12	16	15
14	<11	4
	h01	
2	68	90
4	44	37
6	37	40
8	27	25
10	23	23
12	<12	5
14	11	11
	h02	
0	31	38
2	72	74
4	72	65
6	19	21
8	22	20
10	23	23
12	22	20
14	10	9

h	$\lvert F_o\rvert$	$\lvert F_c\rvert$
	h03	
2	32	34
4	30	24
6	22	20
8	20	18
10	16	14
12	<11	1
	h04	
0	24	26
2	27	28
4	19	19
6	12	10
8	16	15
10	13	12
12	15	14
	h05	
2	20	23
4	<12	3
6	13	11
	h06	
0	23	25
2	11	7

h	$\lvert F_o\rvert$	$\lvert F_c\rvert$
	h10	
1	x	6
2	x	96
3	28	28
4	5	9
5	<5	3
6	25	28
7	25	26
8	10	10
9	8	11
10	<8	6
11	13	17
12	<8	1
13	<8	5
14	<7	4
15	7	5
	h11	
0	x	110
1	60	55
2	54	54
3	52	56
4	17	15
5	45	40
6	18	19
7	21	23
8	21	21

h	$\lvert F_o\rvert$	$\lvert F_c\rvert$
	h11 (cont.)	
9	<7	5
10	17	18
11	13	12
12	14	16
13	11	10
14	8	5
	h12	
1	34	33
2	10	11
3	24	25
4	27	27
5	21	22
6	13	14
7	13	18
8	17	19
9	<8	6
10	14	14
11	<8	6
12	<8	2
	h13	
0	13	9
1	31	34
2	33	34
3	15	16
4	28	30

h	$\lvert F_o\rvert$	$\lvert F_c\rvert$
	h13 (cont.)	
5	7	6
6	8	6
7	11	12
8	<8	3
9	22	21
10	14	13
11	<8	2
12	10	10
	h14	
1	15	18
2	9	6
3	11	12
4	10	11
5	11	13
6	9	7
7	9	6
8	10	10
9	<8	4
10	10	10
	h15	
0	22	26
1	11	8
2	11	9
3	10	9
4	8	5

h	$\lvert F_o\rvert$	$\lvert F_c\rvert$
	h15 (cont.)	
5	9	11
6	<8	3
7	8	5
8	9	6
	h16	
1	7	3
2	9	11
	h17	
0	6	6
	h20	
1	x	28
2	x	11
3	35	33
4	<4	1
5	41	49
6	9	10
7	11	12
8	7	8
9	7	8
10	<7	5
11	16	17
12	8	9
13	14	16

h	$\lvert F_o\rvert$	$\lvert F_c\rvert$
	h21	
1	42	37
2	13	16
3	24	22
4	13	13
5	24	26
6	<6	5
7	9	8
8	11	9
9	12	10
10	9	8
11	10	9
	h22	
0	21	23
1	42	44
2	12	10
3	32	34
4	8	11
5	9	9
6	11	11
7	16	18
8	8	3
9	18	21
10	<7	6
11	9	6

h	$\lvert F_o\rvert$	$\lvert F_c\rvert$
	h23	
1	<6	7
2	15	16
3	16	16
4	9	10
5	<7	4
6	8	5
7	17	19
8	9	8
9	<7	1
10	<7	2
11	7	8
	h24	
0	16	12
1	22	22
2	<7	5
3	18	19
4	10	6
5	<7	7
6	<7	7
7	11	10
8	<7	2
9	9	8
	h25	
1	9	7
2	8	5

The bond lengths and angles in the carboxyl group fall within the range of best values listed in a review concerning the carboxyl group by Davies & Thomas (1950). The four heavy atoms of the molecule are planar within experimental error. The bond lengths and angles are compared with the results of determinations in the gas phase in Table 3. The most noteworthy differences with respect to the electron-diffraction data are the decrease of the C–O bond length in the sequence monomer, dimer, chain, and the shorter hydrogen-bond length in the chain. These differences in the C–O and O–H · · · O bond lengths have also been found in formic acid gas and solid (Karle & Karle, 1954; Holtzberg *et al.*, 1953).

Table 3. *Bond lengths and angles for acetic acid*

	Gas*		Crystal
	Monomer	Dimer	Chain
C=O	1·24±0·03 Å	1·25±0·03 Å	1·24±0·02 Å
C–O	1·43±0·03	1·36±0·04	1·29±0·02
C–C	1·54±0·04	1·54±0·04	1·54±0·02
O–H · · · O	—	2·76±0·06	2·61±0·02
C–C=O	113–128°	120±5°	122±2°
C–C–O	125–94	110±5	116±2
O=C–O	122–138	130±3	122±2

* Karle & Brockway (1944).

Our results for the C–O and C=O bond lengths are within the limits of error assigned by Davies & Sutherland (1938) to their estimates for acetic acid monomer and dimer in solution, based on infra-red spectroscopy.

Fig. 3(*a*) shows a section of the hydrogen-bonded chain which is roughly parallel to the (011) plane. Adjacent molecules in the chain are neither coplanar nor parallel. For comparison a section of the formic acid chain is shown in Fig. 3(*b*).

The hydrogen bond distance of 2·61±0·02 Å is within the range of values reported by Ubbelohde & Gallagher (1955) in their list of hydrogen bond distances in monocarboxylic acids.

The angles between the hydrogen bond and the adjacent oxygen–carbon bonds, 144° and 122°, are considerably larger than the corresponding angles in formic acid, 122° and 114° (Holtzberg *et al.*, 1953). The increase of these angles increases the unit chain length and provides room for the methyl groups, each of which otherwise would be rather crowded with respect to an oxygen atom on the neighboring molecule. This carbon–oxygen distance is calculated as 3·47 Å, slightly greater than the sum, 3·4 Å, of the methyl and oxygen van der Waals radii listed by Pauling (1942). All other intermolecular distances are even longer. The shortest methyl–methyl distances are 3·84 Å.

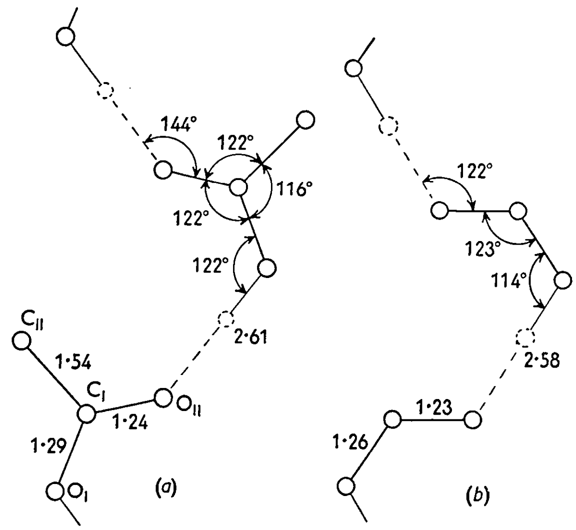

Fig. 3. Molecular dimensions of (*a*) acetic acid, (*b*) formic acid (Holtzberg *et al.*, 1953). Bond lengths are in Ångström units.

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