

Hydrogen Bond Studies

39.* Reinvestigation of the Crystal Structure of Acetic Acid (at +5°C and -190°C)

INGER NAHRINGBAUER

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala 1, Sweden

The crystal structure of acetic acid has been redetermined from two sets of three-dimensional single-crystal X-ray data collected at +5°C and -190°C. The overall structure is the same as that reported in 1958 by Jones and Templeton. The dimensions of the molecule and the hydrogen-bond lengths do not vary with the temperature whereas minor changes occur in the packing of the hydrogen-bonded chains. The two carbon-oxygen distances are significantly different; C=O=1.220(6) Å and C-O(H)=1.318(7) Å at +5°C. Corresponding bond lengths at -190°C are 1.229(5) and 1.319(6) Å. The C-C bond is relatively short, being 1.482(8) Å at +5°C and 1.478(6) Å at -190°C.

The present redetermination of the structure of acetic acid has been undertaken as a complement to a series of structure studies of the hydrogen bonds formed with acetic acid and acetate groups. Primarily the aim has been to improve the precision of the dimensions of the acetic acid molecule. The variation of the bond distances and thermal parameters with temperature is also of great interest. Two independent investigations have thus been made based on single-crystal X-ray data collected at +5°C and -190°C.

The crystal structure of acetic acid was first determined by Jones and Templeton.¹ According to their results the C=O and C-O(H) distances are hardly significantly different ($\Delta=0.05$ Å, $\sigma=0.02$ Å). However, more recent studies of compounds containing unionized carboxyl groups show that the difference is usually at least 0.1 Å. For instance, in the 1:1 addition compound of ammonium acetate and acetic acid, $\text{CH}_3\text{COONH}_4 \cdot \text{CH}_3\text{COOH}$,² the present author found a difference of 0.116 Å. Furthermore, the C-C distance, 1.54 Å, reported by Jones and Templeton is greater than the distance expected for an sp^3-sp^2 carbon-carbon bond. In $\text{CH}_3\text{COONH}_4 \cdot \text{CH}_3\text{COOH}$ an appreciably shorter C-C distance, 1.488 Å, was found for the acetic acid molecule.

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Also of great interest is the polymorphism of acetic acid which has been proposed from a study of the system benzene—acetic acid.³ The existence of two crystalline modifications has recently also been suggested from infrared spectra.⁴ The present work concerns, however, the same modification as that determined by Jones and Templeton. An X-ray study of a single crystal at several temperatures, from +16°C to -190°C, revealed no phase transitions. Attempts to crystallize the proposed second modification are in progress.

EXPERIMENTAL

Water-free acetic acid, obtained by fractional distillation and subsequent repeated recrystallization of commercial acetic acid, was sealed in glass capillaries. A single crystal was grown at +16°C in a low-temperature Weissenberg camera described earlier.⁵ The part of the capillary exposed to the X-rays had a diameter of 0.2 mm and a wall thickness of approximately 0.02 mm.

Multiple-film (five) equi-inclination Weissenberg photographs were taken at +5°C and -190°C using CuK radiation. Four layers, $k=0$ to 3, totally 300 reflexions, were recorded at both temperatures. This corresponds to 75 % of the reflexions within the copper reflexion sphere. The number of reflexions with measurable intensities was 220 at +5°C and 255 at -190°C. The relative intensities of the reflexions, ranging from 1 to 1400, were measured by an automatic SAAB film scanner⁶ on line with an IBM 1800 computer. Processing of transmission values, calculation of integrated intensities and indexing were performed by a program system developed by Werner⁷ at the University of Stockholm. The data were corrected for the Lorentz and polarization effects. No absorption correction was made ($\mu R=0.107$).

UNIT CELL AND SPACE GROUP

Since the diffraction symmetry and systematic absences are in accordance with the observations made by Jones and Templeton¹ their choice of the orthorhombic space group, $Pna2_1$, is assumed to be correct. Accurate dimensions for the unit cell at +5°C and -190°C were obtained from quartz-calibrated zero-layer oscillation photographs around the b and c axes. The cell parameters were fitted to the measured θ values by the method of least squares using the program CELSIUS. References to this and most other programs mentioned in the text have been given in an earlier paper.⁸ The constants used were $a=4.913$ Å for α quartz (25°C), $\lambda(\text{CuK}\alpha_1)=1.54051$ Å, $\lambda(\text{CuK}\alpha_2)=1.54433$ Å, $\lambda(\text{CuK}\beta)=1.39217$ Å. Table 1 shows a comparison of the unit cell dimensions

Table-1. Unit cell dimensions. The standard deviations within parentheses refer to the last digit.

	Jones and Templeton ¹	The present work	
	+5°C	+5°C	-190°C
a	13.32(2) Å	13.310(1) Å	13.214(1) Å
b	4.08(1)	4.090(1)	3.924(1)
c	5.77(1)	5.769(1)	5.766(1)
V	314 Å ³	314.1 Å ³	299.0 Å ³

reported by Jones and Templeton¹ and those obtained in the present work. With four molecules per unit cell, the calculated density is $1.270 \text{ g}\cdot\text{cm}^{-3}$ at $+5^\circ\text{C}$ and $1.334 \text{ g}\cdot\text{cm}^{-3}$ at -190°C . De Visser⁹ reported an observed density of $1.26585 \text{ g}\cdot\text{cm}^{-3}$ at the melting point ($+16.6^\circ\text{C}$).¹⁰

REFINEMENT OF THE STRUCTURE

In order to study possible changes in the structure with temperature both data sets were used in independent series of refinements which were started from the parameters reported by Jones and Templeton.¹ In the first cycles of full-matrix least-squares refinement inter-layer scale factors, coordinates, and isotropic thermal parameters were allowed to vary. When the shifts were about 0.1σ the hydrogen atoms were included with fixed parameters. The coordinates of the hydrogen atoms were obtained from a neutron-

Table 2. Atomic coordinates ($\times 10^4$) and thermal vibration tensor components ($\times 10^4 \text{ \AA}^2$) with standard deviations within parentheses. U_{ij} are coefficients in the expression $\exp[-2\pi^2(h^2a^{-2}U_{11} + \dots + 2hka^{-1}b^{-1}U_{12} + \dots)]$.¹¹

At $+5^\circ\text{C}$									
	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	1287(2)	1075(11)	0	355(18)	523(29)	531(26)	-45(16)	-50(20)	-281(25)
O(2)	2529(3)	3703(9)	1769(12)	409(20)	552(32)	481(21)	-116(16)	59(21)	-203(28)
C(1)	1651(3)	2858(11)	1709(14)	321(23)	209(26)	344(23)	-7(19)	0(23)	-117(29)
C(2)	894(4)	3762(15)	3481(13)	436(28)	412(41)	476(33)	41(22)	152(25)	-120(26)
At -190°C									
O(1)	1269(2)	1130(7)	0	170(11)	229(20)	272(14)	-22(10)	-52(13)	-73(15)
O(2)	2532(2)	3869(5)	1715(9)	148(11)	250(19)	275(13)	-58(8)	0(12)	-82(20)
C(1)	1644(2)	2946(10)	1722(10)	145(14)	115(22)	260(15)	2(11)	-24(21)	21(19)
C(2)	892(3)	3829(11)	3522(9)	175(15)	195(27)	295(21)	20(15)	62(15)	-79(19)

Atomic coordinates ($\times 10^3$) and Debye-Waller factors B (\AA^2) for the hydrogen atoms.

	<i>x</i>	<i>y</i>	<i>z</i>	$B(+5^\circ\text{C})$	$B(-190^\circ\text{C})$		<i>x</i>	<i>y</i>	<i>z</i>	$B(+5^\circ\text{C})$	$B(-190^\circ\text{C})$
H(1)	182	51	-116	4.0	2.0	H(3)	33	540	279	5.0	3.0
H(2)	128	510	491	5.0	3.0	H(4)	53	168	421	5.0	3.0

Table 3. Root-mean-square components R_i (\AA) of thermal displacement along the principal axes of the ellipsoids.

	R_1	At $+5^\circ\text{C}$ R_2	R_3	R_1	At -190°C R_2	R_3
O(1)	0.146(15)	0.197(9)	0.284(12)	0.110(13)	0.147(10)	0.182(9)
O(2)	0.173(15)	0.194(11)	0.277(14)	0.106(10)	0.143(13)	0.187(13)
C(1)	0.119(23)	0.179(7)	0.203(16)	0.105(13)	0.119(9)	0.163(9)
C(2)	0.152(18)	0.215(13)	0.251(14)	0.105(17)	0.143(12)	0.187(11)

Table 4. Observed and calculated structure factors at +5 and -190°C. Reflexions which were too weak to be measured are indicated with one asterisk and these are assigned the intensity I_{min} . Two asterisks indicate reflexions which were excluded from the final refinements.

(+5°C)				(-190°C)				(+5°C)				(-190°C)				(+5°C)				(-190°C)																	
h	k	l	F _o	F _c	F _o	F _c	F _o	F _c	h	k	l	F _o	F _c	F _o	F _c	h	k	l	F _o	F _c	F _o	F _c	h	k	l	F _o	F _c	F _o	F _c	h	k	l	F _o	F _c	F _o	F _c	
2	0	0	22.8	28.7**	23.6	28.2**			2	1	1	13.7	14.6	14.0	15.3	9	2	3	2.4	1.1	*	1.8	1.5	2	2	2	2.6	2.6	2.7	2.7	2	2	2	2.6	2.6	2.7	2.7
4	0	0	19.4	19.6	19.3	20.2			3	1	1	7.0	7.0	6.5	8.2	10	11	12	2.0	2.0	*	2.0	2.0	4	2	2	4.0	4.0	4.2	4.2	4	2	2	4.0	4.0	4.2	4.2
6	0	0	15.1	13.1	17.8	16.3			4	1	1	11.4	12.5	13.7	14.8	11	11	12	2.0	2.0	*	2.0	2.0	5	2	2	2.0	2.0	2.2	2.2	6	2	2	2.0	2.0	2.2	2.2
8	0	0	18.3	18.9	22.3	22.4			5	1	1	2.9	2.7	2.6	2.0	12	13	13	2.0	2.0	*	2.0	2.0	6	2	2	2.0	2.0	2.2	2.2	7	2	2	2.0	2.0	2.2	2.2
10	0	0	10.4	9.8	12.1	11.3			6	1	1	3.0	3.1	4.0	3.9	13	13	13	2.0	2.0	*	2.0	2.0	7	2	2	2.0	2.0	2.2	2.2	8	2	2	2.0	2.0	2.2	2.2
12	0	0	7.4	6.7	10.6	10.5			7	1	1	6.0	5.4	6.0	6.0	14	14	14	2.0	2.0	*	2.0	2.0	8	2	2	2.0	2.0	2.2	2.2	9	2	2	2.0	2.0	2.2	2.2
14	0	0	3.3	3.5	7.3	6.8			8	1	1	2.7	1.8	2.6	2.6	15	15	15	2.0	2.0	*	2.0	2.0	9	2	2	2.0	2.0	2.2	2.2	10	2	2	2.0	2.0	2.2	2.2
16	0	0	2.1	2.0	3.5	3.5			9	1	1	10.1	9.6	10.8	9.5	16	16	16	2.0	2.0	*	2.0	2.0	10	2	2	2.0	2.0	2.2	2.2	11	2	2	2.0	2.0	2.2	2.2
18	0	0	26.9	35.2**	30.8	36.5**			10	1	1	7.0	6.7	9.8	9.5	17	17	17	2.0	2.0	*	2.0	2.0	11	2	2	2.0	2.0	2.2	2.2	12	2	2	2.0	2.0	2.2	2.2
20	0	0	16.4	17.3	16.8	17.0			11	1	1	2.7	1.6	2.3	2.7	18	18	18	2.0	2.0	*	2.0	2.0	12	2	2	2.0	2.0	2.2	2.2	13	2	2	2.0	2.0	2.2	2.2
22	0	0	14.7	15.4	17.1	17.6			12	1	1	2.7	1.6	2.3	2.7	19	19	19	2.0	2.0	*	2.0	2.0	13	2	2	2.0	2.0	2.2	2.2	14	2	2	2.0	2.0	2.2	2.2
24	0	0	11.5	9.8	12.2	10.9			13	1	1	5.7	5.2	6.8	6.8	20	20	20	2.0	2.0	*	2.0	2.0	14	2	2	2.0	2.0	2.2	2.2	15	2	2	2.0	2.0	2.2	2.2
26	0	0	9.5	9.8	12.7	12.3			14	1	1	2.6	3.1	4.2	4.6	21	21	21	2.0	2.0	*	2.0	2.0	15	2	2	2.0	2.0	2.2	2.2	16	2	2	2.0	2.0	2.2	2.2
28	0	0	3.0	3.0	3.3	3.2			15	1	1	1.4	3.0	4.0	4.0	22	22	22	2.0	2.0	*	2.0	2.0	16	2	2	2.0	2.0	2.2	2.2	17	2	2	2.0	2.0	2.2	2.2
30	0	0	9.1	9.1	9.0	9.1			16	1	1	3.6	3.6	4.8	4.8	23	23	23	2.0	2.0	*	2.0	2.0	17	2	2	2.0	2.0	2.2	2.2	18	2	2	2.0	2.0	2.2	2.2
32	0	0	12.2	12.2	12.0	12.5			17	1	1	4.4	4.4	5.6	5.6	24	24	24	2.0	2.0	*	2.0	2.0	18	2	2	2.0	2.0	2.2	2.2	19	2	2	2.0	2.0	2.2	2.2
34	0	0	26.1	29.7	31.2	32.0			18	1	1	5.7	5.6	6.2	6.2	25	25	25	2.0	2.0	*	2.0	2.0	19	2	2	2.0	2.0	2.2	2.2	20	2	2	2.0	2.0	2.2	2.2
36	0	0	25.2	28.2	30.5	30.5			19	1	1	5.5	5.5	5.6	5.6	26	26	26	2.0	2.0	*	2.0	2.0	20	2	2	2.0	2.0	2.2	2.2	21	2	2	2.0	2.0	2.2	2.2
38	0	0	7.6	7.0	7.6	7.0			20	1	1	4.4	4.4	4.8	4.8	27	27	27	2.0	2.0	*	2.0	2.0	21	2	2	2.0	2.0	2.2	2.2	22	2	2	2.0	2.0	2.2	2.2
40	0	0	10.1	9.6	13.1	12.3			21	1	1	3.6	3.6	4.0	4.0	28	28	28	2.0	2.0	*	2.0	2.0	22	2	2	2.0	2.0	2.2	2.2	23	2	2	2.0	2.0	2.2	2.2
42	0	0	11.5	10.8	16.4	15.0			22	1	1	3.6	3.6	3.6	3.6	29	29	29	2.0	2.0	*	2.0	2.0	23	2	2	2.0	2.0	2.2	2.2	24	2	2	2.0	2.0	2.2	2.2
44	0	0	10.7	11.3	16.2	16.0			23	1	1	2.7	2.1	2.1	2.1	30	30	30	2.0	2.0	*	2.0	2.0	24	2	2	2.0	2.0	2.2	2.2	25	2	2	2.0	2.0	2.2	2.2
46	0	0	2.3	2.3	5.6	6.2			24	1	1	4.1	4.1	4.1	4.1	31	31	31	2.0	2.0	*	2.0	2.0	25	2	2	2.0	2.0	2.2	2.2	26	2	2	2.0	2.0	2.2	2.2
48	0	0	13.0	12.1	13.6	14.4			25	1	1	11.8	11.9	15.3	15.1	32	32	32	2.0	2.0	*	2.0	2.0	26	2	2	2.0	2.0	2.2	2.2	27	2	2	2.0	2.0	2.2	2.2
50	0	0	11.7	11.1	12.7	12.8			26	1	1	5.8	4.9	5.8	4.9	33	33	33	2.0	2.0	*	2.0	2.0	27	2	2	2.0	2.0	2.2	2.2	28	2	2	2.0	2.0	2.2	2.2
52	0	0	9.2	8.5	13.0	10.3			27	1	1	4.9	4.9	5.9	5.5	34	34	34	2.0	2.0	*	2.0	2.0	28	2	2	2.0	2.0	2.2	2.2	29	2	2	2.0	2.0	2.2	2.2
54	0	0	9.0	9.0	12.4	12.1			28	1	1	4.6	4.7	6.5	6.5	35	35	35	2.0	2.0	*	2.0	2.0	29	2	2	2.0	2.0	2.2	2.2	30	2	2	2.0	2.0	2.2	2.2
56	0	0	7.1	7.1	11.1	9.9			29	1	1	3.4	3.4	3.7	3.7	36	36	36	2.0	2.0	*	2.0	2.0	30	2	2	2.0	2.0	2.2	2.2	31	2	2	2.0	2.0	2.2	2.2
58	0	0	3.8	3.8	7.8	7.8			30	1	1	2.2	2.2	2.2	2.2	37	37	37	2.0	2.0	*	2.0	2.0	31	2	2	2.0	2.0	2.2	2.2	32	2	2	2.0	2.0	2.2	2.2
60	0	0	3.3	3.3	9.0	9.0			31	1	1	4.6	4.6	6.5	6.5	38	38	38	2.0	2.0	*	2.0	2.0	32	2	2	2.0	2.0	2.2	2.2	33	2	2	2.0	2.0	2.2	2.2
62	0	0	9.0	9.0	11.1	11.1			32	1	1	3.4	3.4	3.7	3.7	39	39	39	2.0	2.0	*	2.0	2.0	33	2	2	2.0	2.0	2.2	2.2	34	2	2	2.0	2.0	2.2	2.2
64	0	0	3.3	3.3	12.4	12.1			33	1	1	2.7	2.7	0.5	0.5	40	40	40	2.0	2.0	*	2.0	2.0	34	2	2	2.0	2.0	2.2	2.2	35	2	2	2.0	2.0	2.2	2.2
66	0	0	7.1	7.1	11.1	9.9			34	1	1	2.7	3.0	3.0	3.0	41	41	41	2.0	2.0	*	2.0	2.0	35	2	2	2.0	2.0	2.2	2.2	36	2	2	2.0	2.0	2.2	2.2
68	0	0	11.5	11.2	12.8	13.2			35	1	1	4.4	4.4	4.7	4.7	42	42	42	2.0	2.0	*	2.0	2.0	36	2	2	2.0	2.0	2.2	2.2	37	2	2	2.0	2.0	2.2	2.2
70	0	0	15.4	14.8	14.5	14.8			36	1	1	2.4	2.4	2.6	2.6	43	43	43	2.0	2.0	*	2.0	2.0	37	2	2	2.0	2.0	2.2	2.2	38	2	2	2.0	2.0	2.2	2.2
72	0	0	11.7	11.6	6.2	6.0			37	1	1	2.3	0.4	1.8	0.8	44	44	44	2.0	2.0	*	2.0	2.0	38	2	2	2.0	2.0	2.2	2.2	39	2	2	2.0	2.0	2.2	2.2
74	0	0	3.7	3.7	6.2	6.0			38	1	1	2.4	2.4	3.6	3.6	45	45	45	2.0	2.0	*	2.0	2.0	39	2	2	2.0	2.0	2.2	2.2	40	2	2	2.0	2.0	2.2	2.2
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diffraction study of acetic acid which is in progress at this Institute.²² Difference synthesis with hydrogen excluded in the F_c calculations indicated approximately the same hydrogen positions as the neutron analysis. After some additional cycles of refinement the thermal parameters of the heavy atoms were subjected to anisotropic refinement. The inter-layer scale factors were then kept fixed. In the final cycles of refinement five and ten reflexions, respectively, were excluded from the data sets. They were all low angle, high intensity reflexions with values of F_o smaller than F_c , possibly due to secondary extinction effects or substantial error in the intensity measurement. The refinements were interrupted when the shifts of the parameters were less than 0.1σ . The final discrepancy indices $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ were 0.065 (+5°C) and 0.053 (-190°C).

Table 2 lists the final atomic coordinates and vibration tensor components U_{ij} . The latter were obtained from the anisotropic thermal parameters β_{ij} according to Scheringer.¹¹ The r.m.s. components of thermal displacement along the principal axes of the ellipsoids are given in Table 3. The observed and calculated structure factors are compared in Table 4.

The Fourier calculations were made using the program DRF. In the least-squares refinements the full-matrix program LALS was used with minimization of $\sum w(|F_o| - |F_c|)^2$. The weights were calculated according to the expression $w = 1/(a + |F_o| + c|F_o|^2 + d|F_o|^3)$. The final values used for a , c , and d were 2.0, 0.1, and 0.01. A weight analysis indicated suitable weighting factors, w . Reflexions too weak to be measured were given zero weight, and were also omitted in all calculations of R values. The atomic scattering factors used are those for neutral O, N, C, and H given in the *International Tables for X-ray Crystallography*.¹² Distances and angles (Tables 5-6, Figs. 3 and 4) were calculated from the atomic coordinates obtained in the final least-squares calculation using the program OR FFE.¹³ The standard deviations were computed from the errors of the atomic parameters in the form of a variance-covariance matrix and from the errors in the cell dimensions. The illustrations were prepared by means of the plot program OR TEP.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The overall structure agrees with that found by Jones and Templeton.¹ As illustrated in Fig. 1 the acetic acid molecules are hydrogen bonded into roughly planar chains. The maximum deviation of the heavy atoms from the least-squares plane is 0.3 Å. The hydrogen-bonded chains are tightly packed in layers parallel to (100). The direction of the chains in the alternating close-packed layers is approximately parallel to [011] and [0 $\bar{1}$ 1], respectively. The interaction between the chains is apparently of van der Waals type.

The acetic acid molecule. The acetic acid molecules are approximately planar at both temperatures. None of the atoms O(1), O(2), C(1), C(2), and H(1) deviate from the least-squares plane by more than 0.006 Å. The bond lengths and angles of the acetic acid molecule in the pure compound and in some addition compounds of acetic acid are compared in Table 5. The dimensions at +5°C and -190°C are equal except for an insignificant difference in the C=O distances.

Table 5. Dimensions of the acetic acid molecule in the solid phase.

	Temp.	C-C	C=O	C-O(H)	C-C=O	C-C-O(H)	O=C-O(H)	Ref.
CH ₃ COOH	-190°C	1.478(6) Å	1.229(5) Å	1.319(6) Å	125.1(5)°	113.8(3)°	121.1(5)°	This work
	+5	1.482(8)	1.220(6)	1.318(7)	124.2(7)	113.8(4)	122.0(6)	*
	+5	1.54(2)	1.24(2)	1.29(2)	122.3(9)	115.6(7)	122.1(10)	1
CH ₃ COONH ₄ ·CH ₃ COOH	-40	1.488(5)	1.209(4)	1.325(5)	125.2(3)	112.4(3)	122.5(3)	2
C ₂ H ₅ N ₂ Cl·CH ₃ COOH	-10	1.470(16)	1.216(8)	1.326(16)	125.5(12)	113.9(7)	120.5(10)	14

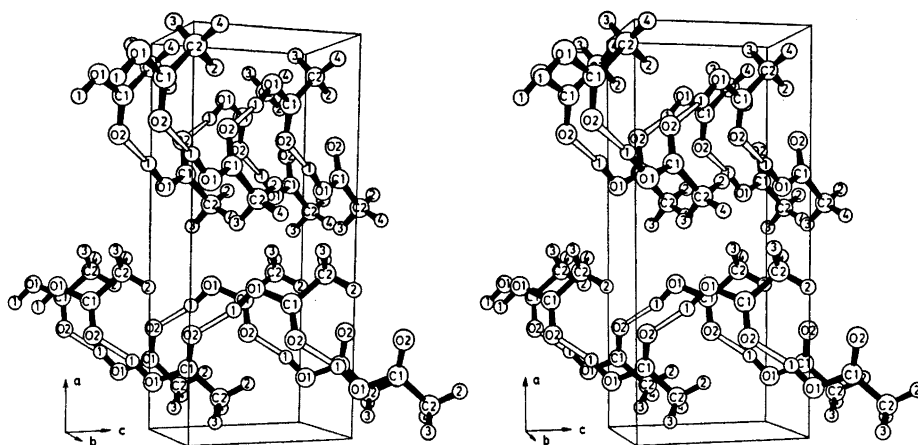


Fig. 1. A stereoscopic pair of drawings showing the structure of acetic acid. Covalent bonds are filled and open bonds represent $O\cdots H$ interaction in a hydrogen bond. The hydrogen atoms are denoted by 1-4.

There are some notable differences between the values obtained and the previously reported values. The precision is improved and the new dimensions are in closer agreement with those in other carboxyl compounds. This means, for example, that the $C=O$ and $C-O(H)$ distances are now significantly different. Furthermore, the $C-C$ distance is appreciably shorter, 1.482 and 1.478 Å as compared with 1.54 Å.

The present dimensions of the acetic acid molecule are very nearly the same as those observed in the 1:1 addition compounds of ammonium acetate and acetic acid² and of benzenediazonium chloride and acetic acid.¹⁴ Also in these compounds the $C-C$ distances, 1.488 and 1.470 Å, are remarkably short as compared with the bond length generally accepted for a single $C-C$ bond of sp^3-sp^2 type. From classifications of experimentally found $C-C$ single bonds according to the type of hybridization, Brown¹⁵ has suggested a value, 1.505 Å, and Dewar and Schmeising¹⁶ have proposed a somewhat longer distance, 1.515 Å. Further examples of $C(sp^3)-C(sp^2)$ bonds significantly shorter than the above mentioned average distances have been observed in the compounds $TiCl_4 \cdot CH_3COOC_2H_5$,¹⁷ $CH_3C(OH)_2HSO_4$,¹⁸ and $CH_3C(OH)_2FSO_3$.¹⁹ The corresponding $C-C$ distances are 1.484, 1.480, and 1.469 Å.

The methyl group. As seen in Fig. 1 one of the methyl hydrogen atoms is in an eclipsed position with respect to the carbonyl oxygen. The same conformation of the substituents about the $C(sp^3)-C(sp^2)$ bond is found in higher aliphatic carboxylic acids,²⁰ i.e. a β -carbon atom has the same position as the methyl hydrogen atom. An investigation by electron diffraction²¹ indicates that the conformation about the $C-C$ bond of acetic acid is unchanged in the gas phase.

The hydrogen bond. The length of the hydrogen bond is, within the experimental errors, the same at $+5^\circ C$ and $-190^\circ C$. Also the angles between the

hydrogen bond and adjacent C=O and C—O(H) bonds are very nearly the same at the two temperatures: 134° and 121° at +5°C, and 132° and 120° at -190°C. In the previous investigation¹ of acetic acid a similar value, 122°, was found for the angle C—O(H)⋯O but by mistake * the angle C=O⋯(H)O was incorrectly reported as 144° rather than 135°. A more detailed discussion of the hydrogen bond will be made in a subsequent report concerning the neutron diffraction study.²²

The acetic acid molecule may be expected to occur in either the *cis* form or the *trans* form (*cf.* Fig. 2). In the present modification of the solid the

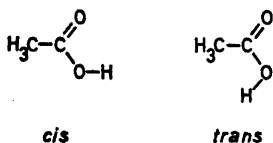


Fig. 2. *cis* and *trans* Configuration of the carboxyl group for acetic acid.

molecule has evidently the *cis* form. From the infrared spectrum of gaseous formic acid²³ the *cis* form is found to be 2 kcal/mole more stable than the *trans* form. It is reasonable to assume that the *cis* form is the more stable conformation in the case of acetic acid as well.

Table 6. The bond distances of acetic acid in the gas and the solid phase. The values for the monomer and the dimer are obtained by electron diffraction²¹ whereas the distances for the solid phase are those derived in the present X-ray study.

	Gas		Solid	
	Mon. +160°C	Dimer +24°C	Chain +5°C	Chain -190°C
C=O	1.212(1) Å	1.230(2) Å	1.220(6) Å	1.229(5) Å
C—O(H)	1.358(1)	1.333(2)	1.318(7)	1.319(6)
C—C	1.515(1)	1.503(2)	1.482(8)	1.478(6)
O(H)⋯O		2.690	2.626(6)	2.625(4)

Comparison between the solid and the gas phase. Table 6 gives a comparison with the results obtained by electron diffraction.²¹ Of special interest from the hydrogen-bond point of view are the significant differences in the dimensions of the carboxyl group. Noteworthy are the decrease of the C—O(H) distance in the sequence monomer, dimer, and chain, and the shorter hydrogen-bond length in the chain as compared with the dimer. Changes in the hydrogen bond are expected to influence the C=O bond less than the C—O(H) bond. It is accordingly not surprising that the C=O distances are not significantly different for the dimer and the chain. On the other hand, the monomer has a slightly shorter C=O bond than the dimer which might be due to its absence of hydrogen bonding. Another interesting effect is the decrease of the C—C

* Private communication.

bond length in the sequence monomer, dimer, and chain. From a comparison of infrared spectra of acetic acid in the gas and the solid phase, *i.e.* as monomer,²⁴ dimer,²⁵ and chain,²⁶ Haurie and Novak observed a correlation between all the skeletal stretching frequencies ($\nu\text{C}=\text{O}$, $\nu\text{C}-\text{O}(\text{H})$, $\nu\text{C}-\text{C}$) and the νOH frequency. They noticed that a stronger hydrogen bond implies a decrease of $\nu\text{C}=\text{O}$ and an increase of $\nu\text{C}-\text{C}$ as well as of $\nu\text{C}-\text{O}(\text{H})$.

Comparison of the structure at +5°C and -190°C. The change of the cell dimensions with temperature is evidently anisotropic (*cf.* Table 1). When the temperature is lowered the *c* parameter is hardly affected whereas the *a* and the *b* parameters are decreased by about 1 and 5 %, respectively. Since the dimensions of the molecule and the hydrogen-bond system remain nearly unchanged the predominant changes occur in the packing of the hydrogen-bonded chains.

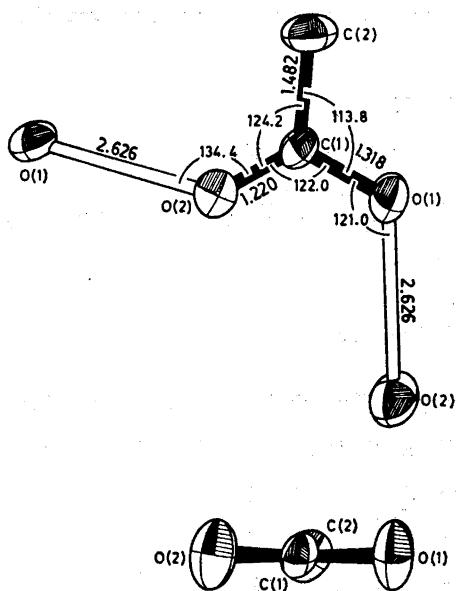


Fig. 3. Bond distances and angles involving the heavy atoms of acetic acid at +5°C. Thermal ellipsoids are scaled to include 50 % probability. The upper figure shows the molecule viewed perpendicular to the plane of the molecule. The lower figure gives a view along the plane of the molecule, perpendicular to the O—O line.

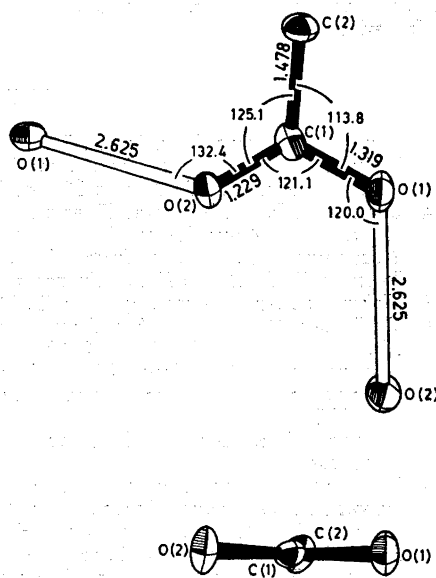


Fig. 4. Bond distances and angles involving the heavy atoms of acetic acid at -190°C. Additional notation is the same as in Fig. 2.

When the temperature is lowered from +5°C to -190°C the size of the thermal ellipsoids is changed. The principal axes are shortened by 25 to 40 % for O(1), O(2), and C(2) whereas in the case of C(1) the decrease is only 10 % for the shortest axis and 20 % for the longest one (*cf.* Table 3). Regarding

the anisotropy of the thermal motion and the directions of the principal axes there are no drastic changes with temperature except for C(1) (Fig. 3 and 4). Since the thermal parameters may be slightly in error due to lack of experimental scaling *etc.*, no detailed discussion is justified. However, at both temperatures the largest amplitude of the motion for the oxygen atoms is apparently approximately perpendicular to the molecular plane.

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