

## Hydrogen Bond Studies. XLIV.\* Neutron Diffraction Study of Acetic Acid†

BY PER-GUNNAR JÖNSSON‡

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, U.S.A.

(Received 15 April 1970 and in revised form 1 November 1970)

The crystal structure of acetic acid has been refined from three-dimensional neutron diffraction data recorded at  $-140^{\circ}\text{C}$ . The crystals are orthorhombic, space group  $Pna2_1$ , with four molecules of  $\text{CH}_3\text{COOH}$  in a unit cell of dimensions  $a = 13.225$  (9),  $b = 3.963$  (3),  $c = 5.762$  (3) Å. The acetic acid molecules are connected by hydrogen bonds to form infinite chains. The carbonyl oxygen accepts a hydrogen bond from the hydroxyl group of a neighboring molecule, the hydrogen bond lengths are  $\text{H}\cdots\text{O}$  1.642 (13) and  $\text{O}\cdots\text{O}$  2.631 (8) Å, the  $\text{O}-\text{H}\cdots\text{O}$  angle is  $164.8^{\circ}$ . The intramolecular bond distances are  $\text{C}-\text{O}$  1.321 (7),  $\text{C}=\text{O}$  1.206 (8),  $\text{C}-\text{C}$  1.501 (7),  $\text{O}-\text{H}$  1.011 (15) and the mean  $\text{C}-\text{H}$  distance is 1.060 (10) Å. The above distances were not corrected for thermal motion.

### Introduction

The crystal structure of acetic acid was determined by Jones & Templeton (1958) (referred to as JT below) from X-ray diffraction data recorded at  $+5^{\circ}\text{C}$ . In a study concurrent with the work reported here, Nahringsbauer (1970) has carried out a redetermination of the structure at  $+5^{\circ}$  and  $-190^{\circ}\text{C}$  using X-ray film data evaluated by an automatic film scanner. This paper reports the structure of acetic acid as studied by neutron diffraction at  $-140^{\circ}\text{C}$ .

### Crystal data

Acetic acid,  $\text{CH}_3\text{COOH}$ . F.W. 60.05, m.p.  $16.6^{\circ}\text{C}$ .

Orthorhombic,  $a = 13.225$  (9),  $b = 3.963$  (3),

$c = 5.762$  (3) Å,

$V = 302.0$  Å<sup>3</sup> at  $-140^{\circ}\text{C}$ .

(Neutron radiation,  $\lambda = 0.826$  (2) Å).

$D_m^{183} = 1.326$  g.cm<sup>-3</sup> (Bilz, Fischer & Wünnenberg, 1930),

$Z = 4$ ,

$D_c^{140} = 1.321$  g.cm<sup>-3</sup>.

Space group  $Pna2_1$ .

Calculated neutron absorption coefficient:  $1.80$  cm<sup>-1</sup>.

### Experimental

Water-free reagent-grade acetic acid was sealed in a thin-walled quartz tube. A single crystal was grown at a temperature near its melting point in a modified precession camera. The camera carried a tube for passing a stream of cold air parallel to the axis of the quartz tube. The acetic acid crystals had a tendency to grow

very rapidly in thin needles resulting in a number of differently oriented crystallites. Constant attention was therefore needed; as soon as a rapidly growing needle began to form it was remelted. The cylindrical single crystal finally obtained had a volume of  $3.85$  mm<sup>3</sup>; its radius was  $0.60$  mm. The quality of the crystal was checked by taking precession X-ray photographs using Mo *K* radiation. The cell dimensions were found to be in reasonable agreement with the values of JT. With the crystal immersed in a cold bath, the goniometer head was transferred to the Brookhaven High Flux Beam Reactor. It was mounted on a four-circle neutron diffractometer equipped with the ALTA low-temperature apparatus (Rudman & Godel, 1969). The temperature was maintained at  $-140 \pm 1^{\circ}\text{C}$  by blowing a cold stream of nitrogen gas over the crystal. The crystal was aligned about an axis normal to the (211) planes. This direction coincided closely with the axis of the quartz tube. Ten reflections were carefully centered manually and their  $2\theta$  values recorded. Cell dimensions together with standard deviations were obtained by a least-squares procedure, the results of which are given above. The neutron wavelength was  $0.826$  (2) Å. The uncertainty in the wavelength was not included in the calculation of the standard deviations. However, it is reassuring to note the good agreement with the values of Nahringsbauer (1970) when these values are interpolated to  $-140^{\circ}\text{C}$ .

Intensity data were collected at  $-140^{\circ}\text{C}$  using the computer-controlled Multiple Spectrometer Control System (Beaucage, Kelley, Ophir, Rankowitz, Spinrad & van Norton, 1966). Using a  $\theta-2\theta$  step scan technique a portion of reciprocal space extending out to  $\sin \theta/\lambda = 0.76$  Å<sup>-1</sup> was examined. During the data collection it was noticed that certain reflections were considerably miscentered. This error could be traced to an unfavorably shaped goniometer head for which, in certain orientations, one of the arcs moved into the path of the cold stream. The uneven cooling which resulted caused a temporary missetting of the crystal. This source of error could not be completely avoided

\* Part XLIII: *Acta Chem. Scand.* (1971), **25**, 189.

† Research performed under the auspices of the U.S. Atomic Energy Commission.

‡ Present address: Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala 1, Sweden.

§ Numbers in parenthesis here and throughout this paper are the estimated standard deviations in the least significant digits.

Table 1. Final positional and thermal parameters for acetic acid

The positional parameters are given as fractional coordinates  $\times 10^4$ . The vibration tensor components (in  $10^4 \text{ \AA}^2$ ) are defined as  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ . The second line given for each heavy atom parameter compares the neutron results with the X-ray results of Nahrungbauer (interpolated to  $-140^\circ\text{C}$ , see text). The value given first is  $\Delta$  (defined as the interpolated X-ray parameter value minus the neutron parameter value) followed by  $|\Delta|/\sigma$ , where  $\sigma$  is the combined standard deviation (see text).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
O(1)	1275 (5) -1 0.2	1096 (16) 20 1.1	0	268 (35) -51 1.4	322 (26) -18 0.5	244 (25) 94 3.1	-19 (22) -9 0.4	15 (31) -66 1.9	-109 (25) -17 0.6
O(2)	2523 (4) 8 1.8	3850 (13) -24 1.7	1707 (15) 22 1.2	193 (30) 22 0.7	371 (25) -44 1.3	201 (18) 127 5.4	-44 (20) -29 1.3	3 (27) 12 0.4	-71 (28) -42 1.2
C(1)	1649 (4) -3 0.7	2978 (10) -55 3.9	1685 (14) 34 1.9	184 (25) 6 0.2	238 (16) -99 3.5	157 (15) 125 5.5	13 (16) -13 0.6	5 (23) -23 0.7	-36 (20) 22 0.7
C(2)	884 (4) 9 1.8	3840 (13) -28 1.6	3519 (13) -8 0.5	288 (33) -46 1.2	281 (22) -30 0.8	252 (20) 89 2.8	-41 (20) 66 2.5	41 (22) 44 1.5	-73 (23) -17 0.5
H(1)	1820 (9)	511 (28)	-1163 (20)	359 (65)	427 (57)	269 (41)	15 (39)	-102 (50)	-88 (39)
H(2)	1277 (13)	5102 (57)	4910 (25)	776 (114)	1046 (126)	419 (74)	-320 (89)	168 (82)	-409 (86)
H(3)	327 (12)	5402 (62)	2786 (33)	636 (132)	1305 (165)	532 (83)	401 (133)	189 (82)	104 (95)
H(4)	531 (19)	1683 (39)	4207 (46)	1432 (177)	418 (84)	944 (123)	-189 (91)	547 (141)	-30 (82)

since there was no simple means of restricting the  $\phi$  motion of the diffractometer. Instead, the affected reflections were later identified by inspection of the recorded peak profiles and removed from the data set. About 100 reflections had to be rejected for this reason. Due to early shut-down of the reactor no reflections with  $h$  larger than 13 were recorded.

The data were corrected for background and assigned standard deviations based on Poisson counting statistics. Values of  $F^2$  and  $\sigma_{\text{count}}(F^2)$  were then calculated by applying the Lorentz factor and absorption corrections to the values of  $I$  and  $\sigma(I)$ . The cylindrical shape of the crystal was represented approximately by 38 boundary planes in the calculation of the absorption correction. The resulting transmission factors fell in the range 0.81–0.84. The linear absorption coefficient of  $1.80 \text{ cm}^{-1}$  was calculated using a value of 34 barns for the incoherent scattering cross-section for hydrogen.

### Location of the hydrogen atoms and refinement

A three-dimensional difference map, for which the calculated structure factors were based on the parameters given by JT, revealed the positions of the hydrogen atoms. The structure was refined using the full-matrix least-squares program *LINUS*. The function minimized was  $\sum w(|F_o| - |F_c|)^2$ . Only reflections with  $F^2$  values larger than  $\sigma(F^2)$  were included; the total number of reflections was 316. Each reflection was assigned a weight  $w$  inversely proportional to the estimated variance of the observation

$$w^{-1} = \sigma^2(F) = \sigma^2(F^2)/4F^2$$

and

$$\sigma^2(F^2) = \sigma_{\text{count}}^2(F^2) + k^2F^4$$

where  $k$  was 0.10 and  $\sigma_{\text{count}}^2$  was based on counting statistics alone.

The parameters refined were 23 positional parameters, 48 anisotropic thermal parameters and an overall scale factor. No correction for secondary extinction was needed. In the last cycle of least-squares refinement no

parameter shifted by more than  $0.1\sigma$ ; the final agreement factors were

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.075$$

and

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.092.$$

Table 2. Observed and calculated neutron structure amplitudes for acetic acid

The four columns are, in order, the indices  $k$  and  $l$ ,  $100|F_o|$  and  $100|F_c|$  (in units of  $10^{-12} \text{ cm}$ ).

*** H <sup>o</sup> ***	3 2 232 223	3 4 156 157	3 3 147 148	4 2 41 64
0 2 557 505	3 5 95 100	3 6 172 155	3 5 244 234	5 0 91 92
0 4 311 299	3 5 65 65	3 7 78 58	4 0 247 232	2 0 86 107
0 6 640 619	4 0 67 62	4 0 39 46	4 1 70 81	*** H <sup>10</sup> ***
1 5 490 473	4 3 232 243	4 1 139 138	5 1 109 88	0 0 166 165
1 7 214 237	4 4 102 106	4 2 255 261	4 3 39 47	0 1 522 486
2 0 323 295	5 2 87 80	4 3 39 47	4 4 132 151	0 1 145 117
2 2 102 122	4 4 122 120	4 5 122 120	*** H <sup>7</sup> ***	1 1 250 256
2 4 166 179	*** H <sup>3</sup> ***	1 0 329 315	1 3 57 52	1 1 229 250
3 1 219 216	1 0 64 62	1 1 317 331	1 3 97 92	2 0 55 51
4 0 108 116	1 1 262 275	1 2 205 232	1 3 97 92	2 1 204 150
6 0 68 66	1 2 307 315	1 0 73 66	1 5 145 157	2 2 97 101
*** H <sup>1</sup> ***	1 3 293 282	1 1 108 120	1 7 67 69	3 0 204 163
1 1 189 204	1 4 249 242	1 2 111 250	1 3 97 92	3 1 109 111
1 2 217 208	1 5 74 87	1 3 133 151	2 2 134 139	3 2 110 119
1 3 265 241	1 6 109 107	1 4 175 162	2 3 249 294	3 3 91 94
1 4 409 385	1 7 191 196	1 5 195 190	2 4 116 130	4 1 109 103
1 5 210 197	1 8 69 74	1 8 108 92	2 7 70 39	4 2 165 125
1 6 128 122	2 1 40 38	2 0 370 354	3 1 71 84	*** H <sup>11</sup> ***
1 7 180 169	2 2 352 406	2 1 187 179	3 2 187 179	0 0 463 411
1 8 87 60	2 3 284 277	2 2 56 74	4 0 106 105	0 1 250 255
2 0 444 404	2 4 279 256	2 3 167 163	4 1 116 121	1 1 369 319
2 1 400 401	2 5 109 98	2 4 85 84	4 2 152 149	1 3 85 88
2 2 236 236	2 6 131 115	2 5 123 117	5 1 168 180	2 0 363 333
2 3 104 107	2 8 165 148	2 7 172 186	*** H <sup>8</sup> ***	2 1 166 143
2 4 386 416	3 1 239 233	3 0 58 42	0 0 343 316	2 2 185 80
2 5 136 140	3 2 222 226	3 2 155 162	0 1 294 281	2 3 119 113
2 6 178 180	3 3 105 125	3 3 131 149	0 2 106 108	2 4 153 178
2 7 153 143	3 4 76 87	3 4 106 111	0 3 345 402	3 1 171 172
2 8 125 130	3 5 95 89	3 5 109 63	0 4 123 123	3 2 222 219
3 0 236 236	3 6 129 134	3 6 86 93	0 5 182 191	3 3 132 125
3 1 305 301	4 1 205 180	4 1 115 119	1 0 68 67	3 1 191 179
3 2 84 85	4 2 84 71	4 2 204 202	1 1 136 136	3 3 128 137
3 3 199 236	5 0 171 156	5 0 104 95	1 2 293 340	4 0 98 69
3 6 82 85	5 1 113 131	5 1 225 218	1 102 204	4 3 85 74
3 7 134 128	5 2 133 126	5 2 87 98	1 5 118 116	*** H <sup>12</sup> ***
4 1 92 92	5 3 99 99	5 3 59 62	2 0 90 102	2 1 199 195
4 2 152 157	5 4 100 114	5 4 100 114	2 2 40 69	0 0 486 428
*** H <sup>4</sup> ***	0 0 280 257	*** H <sup>6</sup> ***	2 3 137 160	0 1 161 155
0 0 421 388	0 1 251 254	0 0 317 302	2 6 79 79	0 2 387 405
0 1 500 493	0 2 215 224	0 1 324 305	0 2 218 202	0 3 113 111
0 2 448 425	0 3 243 236	0 2 283 341	0 3 247 250	0 4 309 340
0 3 399 358	0 4 263 189	0 3 251 238	3 2 65 67	0 6 250 270
0 4 317 309	0 5 173 166	0 4 228 244	0 4 128 132	1 1 369 319
0 5 613 578	0 6 107 97	0 5 172 174	3 5 132 136	1 5 281 269
0 6 204 190	0 7 180 172	0 6 158 160	4 0 158 158	2 0 117 112
0 7 115 111	1 0 92 81	1 0 281 253	4 0 232 194	3 1 245 259
0 8 253 243	1 1 112 95	1 1 118 115	4 1 130 135	3 2 103 113
1 0 452 425	1 2 243 245	1 2 137 171	4 2 89 115	3 1 135 153
1 1 241 229	1 3 273 255	1 3 188 201	4 3 87 69	4 0 105 104
1 2 112 96	1 4 266 253	1 4 83 81	5 0 63 37	4 2 142 126
1 3 296 286	1 5 157 139	1 5 72 63	*** H <sup>9</sup> ***	*** H <sup>13</sup> ***
1 4 105 102	1 6 109 96	1 6 90 96	1 0 267 225	1 0 182 143
1 5 213 206	1 8 171 160	1 7 117 120	1 1 51 59	1 1 205 198
1 6 317 303	2 0 149 141	1 8 40 60	2 0 218 202	2 0 451 425
1 7 159 148	2 1 120 118	2 0 341 335	2 1 221 220	2 1 80 87
2 0 132 133	2 2 69 86	2 1 135 145	2 2 153 152	2 2 206 204
2 1 112 96	2 3 194 194	2 2 123 139	2 3 93 91	3 1 206 204
2 2 49 46	2 4 203 180	2 3 103 124	3 2 144 159	4 1 48 41
2 3 320 314	2 5 107 98	2 4 180 211	3 3 152 139	4 2 84 94
2 4 139 144	2 6 110 98	2 5 75 53	3 4 139 139	
2 5 139 144	2 7 147 150	2 6 134 139	3 5 66 66	
2 6 97 90	2 8 345 322	2 7 53 66	3 6 152 159	
2 7 103 98	3 0 195 90	3 0 171 157	3 7 152 159	
3 0 159 129	3 2 157 148	3 1 285 280	3 8 162 202	
3 1 159 61	3 3 333 367	3 2 141 148	4 1 130 132	

The error in an observation of unit weight was 1.53. The final positional and thermal parameters are presented in Table 1. The observed and calculated structure factor amplitudes are listed in Table 2; only those observations used in the refinement are included in the Table. The neutron scattering lengths used were  $b_{\text{O}} = 0.58$ ,  $b_{\text{C}} = 0.665$ ,  $b_{\text{H}} = -0.372$  ( $10^{-12}$  cm).

### Computer programs

Most of the calculations were carried out on the CDC 6600 computer at the Brookhaven National Laboratory. The following programs from the BNL crystallographic program library were used: *CELDIM* for least-squares calculations of cell parameters from observed  $2\theta$  values, *DATAPH* for absorption correction, *FORDAP* for Fourier calculations, *LINUS* for least-squares refinement (Coppens & Hamilton, 1970), *NANOVA* for analysis of the weighting scheme at the end of the least squares refinement, and *ORFFE* (Busing, Martin & Levy, 1964) and *ORTEP* (Johnson, 1965) for structure description.

### Comparison of neutron and X-ray parameters

The only striking discrepancy which appears from a comparison of bond lengths and angles found by Nahringerbauer and JT arises in the angle  $\text{C}(1)\text{--O}(2)\cdots\text{O}(1)$ . The value of JT has since, however, been shown to be incorrectly calculated; it should be  $135^\circ$  rather than  $144^\circ$ . A comparison of the positional and thermal parameters for the heavy atoms with the results of Nahringerbauer is included in Table 1. The X-ray structure

determination was carried out at both  $+5$  and  $-190^\circ\text{C}$ ; the two data sets were refined separately. The X-ray results in Table 1 have been interpolated to correspond to  $-140^\circ\text{C}$  assuming a linear temperature dependence. The Table gives the difference  $\Delta$  (defined as X-ray parameter minus neutron parameter) followed by  $|\Delta|/\sigma$  where  $\sigma$  is the combined standard deviation defined as

$$\sigma = (\sigma_{\text{X-ray}}^2 + \sigma_{\text{neutron}}^2)^{1/2}.$$

The agreement between the positional parameters is satisfactory; the only error greater than twice the combined standard deviation is for the  $y$  coordinate of C(1). The hydrogen atom positions were not refined in the X-ray study; they were constrained to take the values found in the present neutron study. This should not have any appreciable effect on the heavy atom parameters.

Table 3. Bond lengths ( $\text{\AA}$ ) and angles

(a) Bond lengths  
Distances in square brackets are corrected for thermal riding motion.

	Neutron	X-ray*
C(1)---O(1)	1.321 (7) [1.330]	1.319 (6)
C(1)---O(2)	1.206 (8) [1.215]	1.226 (5)
C(1)---C(2)	1.501 (7)	1.479 (7)
C(2)---H(2)	1.078 (14) [1.139]	
C(2)---H(3)	1.050 (20) [1.119]	
C(2)---H(4)	1.052 (17) [1.140]	
O(1)---H(1)	1.011 (15) [1.014]	
O(2)···H(1)	1.642 (13)	
O(1)···O(2)	2.631 (8)	2.624 (5)
O(2)···H(2)	2.409 (15)	
C(2)···O(2)	3.429 (8)	

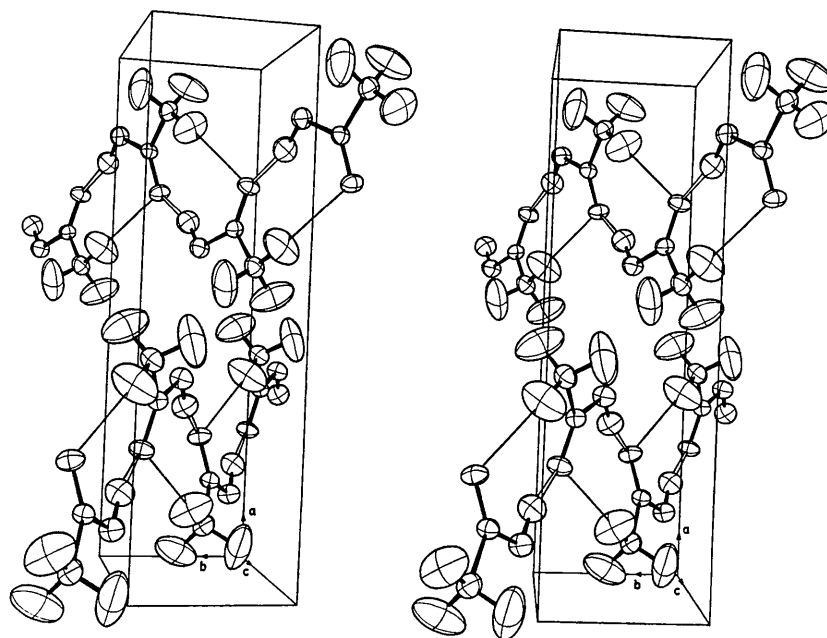


Fig. 1. Stereoscopic illustration of the structure of acetic acid. Thermal ellipsoids are scaled to include 50% probability. Covalent bonds are filled, hydrogen bonds are open and the short intermolecular  $\text{H}\cdots\text{O}$  contacts are indicated by single lines.

Table 3 (cont.)

(b) Angles

	Neutron	X-ray*
O(1)–C(1)—O(2)	121.9 (0.5)	121.3 (0.5)°
C(2)–C(1)—O(1)	113.2 (0.5)	113.8 (0.3)°
C(2)–C(1)—O(2)	124.9 (0.5)	124.9 (0.5)°
C(1)–C(2)—H(2)	107.7 (0.9)	
C(1)–C(2)—H(3)	108.9 (1.0)	
C(1)–C(2)—H(4)	112.3 (1.2)	
H(2)–C(2)—H(3)	111.3 (1.9)	
H(2)–C(2)—H(4)	108.1 (1.9)	
H(3)–C(2)—H(4)	108.6 (2.0)	
C(1)–O(1)—H(1)	110.5 (0.8)	
O(1)–H(1)···O(2)	164.8 (1.0)	
C(1)–O(2)···H(1)	129.1 (0.6)	
C(2)–H(2)···O(2)	157.4 (1.3)	
C(1)–O(2)···H(2)	116.8 (0.6)	

\* The results of Nahrngbauer (1970) interpolated to  $-140^{\circ}\text{C}$ .

Bond lengths and bond angles are compared in Table 3; the X-ray values are interpolated to the temperature of the neutron investigation. The agreement between the X-ray and neutron thermal parameters is less satisfactory than that for the positional parameters. This should not be surprising since it is well known that systematic errors affect thermal parameter values determined by X-rays when a spherical atomic electron distribution is assumed (Hamilton, 1969; Coppens, 1969).

The interpolation employed in correlating the neutron and X-ray results is likely to introduce errors which will appear in the thermal parameters rather than in the positional parameters. In addition, the absence of experimental scaling in the X-ray study may have affected the thermal parameters, so that a more detailed comparison of the thermal parameters is not justified here.

## Discussion of the structure

The structure is illustrated in Fig. 1. Bond lengths and angles are given in Table 3 and in Fig. 2. The acetic acid molecules are joined by  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds forming infinite chains. A description and discussion of the heavy atom geometry has been given by Nahrngbauer and the discussion here will therefore deal mainly with the hydrogen atoms.

*The acetic acid molecule*

The heavy atoms of the acetic acid molecule are coplanar and the hydroxyl hydrogen atom H(1) does not deviate significantly from the plane. The equations for three least-squares planes calculated according to Hamilton (1961) are listed in Table 4. The deviations of all atoms in a given acetic acid molecule and of certain atoms in a neighboring molecule in the same hydrogen bonded chain are also listed.

The conformation of the methyl group can be seen from Fig. 3. The torsion angle  $\text{H}(2)-\text{C}(2)-\text{C}(1)=\text{O}(2)$  is  $-6.3(1.6)^{\circ}$ . A similar conformation exists in the higher aliphatic carboxylic acids, where in almost every case the torsion angle  $\text{C}_{\beta}-\text{C}_{\alpha}-\text{C}=\text{O}$  is found to be close to zero (Kanters, Kroon, Peerdeman & Schoone, 1967; Dunitz & Strickler, 1968).

The mean uncorrected C–H bond length is 1.060 (10) Å. This value is significantly shorter than the commonly accepted value of 1.09 Å. It is clear from Fig. 3 that the methyl group is undergoing a large amplitude torsional vibration about the C–C bond. The root-mean-square displacements along the principal axes of the thermal ellipsoids are given in Table 5. A correction for thermal riding motion (Busing & Levy, 1964) where the hydrogen atoms are assumed to 'ride' on the carbon atom leads to bond lengths which are clearly too long

Table 4. *Least-squares planes for acetic acid and distances of atoms from these planes*

Equations for the planes are of the form  $Ax + By + Cz - D = 0$ , where  $x, y, z$  are fractional coordinates of the unit cell axes  $a, b$  and  $c$ , and  $D$  is the distance of the plane from the origin in Å. Atoms not in the asymmetric unit are specified by a subscript as explained in Table 5.

	Atoms defining plane	Equation
I	O(1), O(2), C(1), H(1)	$3.132x - 3.256y + 2.988z - 0.0467 = 0$
II	O(1), O(2), C(1), C(2), H(1)	$3.252x - 3.268y + 2.935z - 0.0611 = 0$
III	O(1), O(2), C(1), C(2)	$3.240x - 3.278y + 2.913z - 0.0520 = 0$

## Displacements from plane (Å)

	Plane I	Plane II	Plane III
O(1)	-0.004 (6)	-0.005 (6)	0.002 (6)
O(2)	0.000 (7)	0.002 (7)	0.000 (7)
C(1)	0.004 (6)	-0.003 (6)	-0.003 (6)
C(2)	0.031	0.004 (6)	0.001 (6)
H(1)	0.009 (11)	0.022 (11)	0.031
H(2)	0.159	0.128	0.119
H(3)	-0.870	-0.902	-0.905
H(4)	0.829	0.796	0.794
O(1) <sub>5553</sub>	0.629	0.626	0.613
O(2) <sub>5553</sub>	-0.148	-0.179	-0.197
C(1) <sub>5553</sub>	0.403	0.384	0.366
C(2) <sub>5553</sub>	0.910	0.889	0.865
H(1) <sub>5553</sub>	0.302	0.298	0.289

(see Table 3). Such overcorrection has been noted earlier for a methyl group undergoing a very large amplitude of vibration about its threefold axis (Sequeira, Berkeley & Hamilton, 1968).

Table 5. *Root-mean-square amplitudes of vibration (in units of  $10^{-3}$  Å)*

	Axis 1	Axis 2	Axis 3
O(1)	129 (10)	163 (11)	201 (8)
O(2)	129 (11)	139 (12)	201 (8)
C(1)	119 (8)	136 (10)	159 (7)
C(2)	138 (8)	159 (9)	194 (8)
H(1)	136 (16)	194 (16)	222 (13)
H(2)	147 (19)	241 (19)	380 (22)
H(3)	186 (23)	245 (22)	390 (27)
H(4)	192 (20)	248 (22)	425 (27)

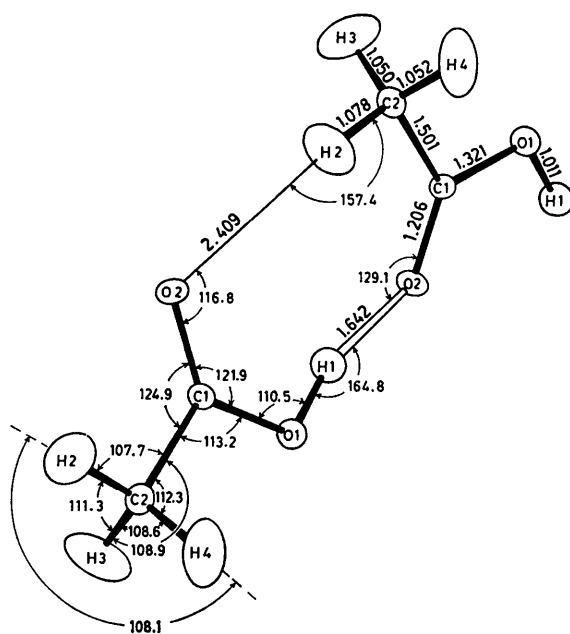


Fig. 2. Bond distances and angles.

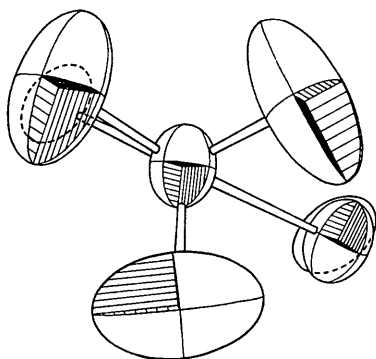


Fig. 3. The acetic acid molecule viewed along the C-C bond. The ellipsoids are scaled to include 50% probability.

### Hydrogen bonding

The O-H...O hydrogen bond has an O...O separation of 2.631 (8) Å, the H...O distance is 1.642 (13) Å and the O-H bond length is 1.011 (15) Å. The hydrogen bond is bent, the O-H...O angle being 164.8 (1.0)°. In the absence of previously reported neutron diffraction results on monocarboxylic acids there is no accurate information available on the exact geometry of the hydrogen bonds in this class of compound. The O...O distance agrees closely with earlier reported values for propionic (Strieter, Templeton, Scheuerman & Sass, 1962), butyric (Strieter & Templeton, 1962) and valeric acid (Scheuerman & Sass, 1962), where O...O distances of 2.62–2.645 Å were found. The structures of these acids take the form of hydrogen bonded dimers, in contrast with the infinite hydrogen bonded chains in the present structure.

Hamilton (1968) has suggested as a criterion for hydrogen bonding that the distance between the hydrogen atom and the possible acceptor atom be at least 0.2 Å shorter than the sum of the van der Waals radii. This sum may be taken as 2.6 Å for hydrogen and oxygen (Pauling, 1960), so that any contacts closer than about 2.4 Å should be considered as possible hydrogen bonds. An examination of Table 6, which gives a list of close intermolecular contacts, reveals one such contact in addition to the hydrogen bond discussed above. This contact is drawn in Fig. 1 as a single line between the methyl hydrogen H(2) and the carbonyl oxygen. The H...O separation is 2.409 (15) Å and the corresponding C...O distance is 3.429 (8) Å; the C-H...O angle is 157.4 (1.3)°. Without conclusive spectroscopic evidence this situation should not be regarded as constituting a C-H...O hydrogen bond, since it is unlikely that the methyl group has sufficient proton-donor ability to form C-H...O bonds (*cf.* Allerhand & Schleyer, 1963).

Table 6. *Short intermolecular distances*

All intermolecular distances involving hydrogen atoms  $\leq 3.0$  Å and not involving hydrogen atoms  $\leq 3.5$  Å, are listed. Atoms not in the asymmetric unit are accompanied by a subscript. The four-digit subscript indicates how the atomic parameters can be derived from the corresponding atom in the asymmetric unit. The first three digits code a lattice translation, *e.g.* 564 means a translation of  $(5-5)a + (6-5)b + (4-5)c$  or  $(b-c)$ . The fourth digit specifies one of the following operations:

- 1:  $x, y, z$
- 2:  $-x, -y, \frac{1}{2} + z$
- 3:  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$

O(1) ... O(2) <sub>5443</sub>	2.631 (8)
O(1) ... H(4) <sub>5542</sub>	2.669 (21)
O(1) ... H(3) <sub>5642</sub>	2.836 (18)
O(1) ... C(1) <sub>5451</sub>	3.397 (9)
O(1) ... O(2) <sub>5451</sub>	3.455 (9)
O(2) ... H(1) <sub>5553</sub>	1.642 (13)
O(2) ... H(2) <sub>5443</sub>	2.409 (15)
O(2) ... C(2) <sub>5543</sub>	3.424 (8)
O(2) ... C(2) <sub>5443</sub>	3.429 (8)
O(2) ... C(1) <sub>5553</sub>	3.479 (7)
O(2) ... O(2) <sub>5553</sub>	3.407 (2)
C(1) ... H(1) <sub>5553</sub>	2.578 (13)

Table 6 (cont.)

C(2)···H(3) <sub>5652</sub>	2·951 (20)
H(1)···H(2) <sub>5443</sub>	2·598 (20)
H(1)···H(2) <sub>5541</sub>	2·991 (25)
H(2)···H(3) <sub>5652</sub>	2·699 (25)
H(2)···H(4) <sub>5651</sub>	2·818 (32)
H(3)···H(4) <sub>5642</sub>	2·622 (27)
H(3)···H(4) <sub>5651</sub>	2·634 (31)

I would like to thank Dr Walter C. Hamilton for the facilities put at my disposal and for his helpful advice. I am also indebted to Sam J. La Placa for his invaluable assistance during the most critical phase of the experiment and to Prof. Ivar Olovsson for his interest in this work.

#### References

- ALLERHAND, A. & SCHLEYER, P. VON R. (1963) *J. Amer. Chem. Soc.* **85**, 1715.
- BEAUCAGE, D. R., KELLEY, M. A., OPHIR, D., RANKOWITZ, S., SPINRAD, R. J. & NORTON, R. VAN (1966). *Nucl. Instrum. Methods* **40**, 26.
- BILZ, W., FISCHER, W. & WÜNNENBERG, E. (1930). *Z. Physik. Chem.* **A151**, 13.
- BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- COPPENS, P. (1969). *Acta Cryst.* **A25**, 180.
- COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71.
- DUNITZ, J. D. & STRICKLER, P. (1968). *Structural Chemistry and Molecular Biology*, Edited by A. RICH & N. DAVIDSON, p. 595. San Francisco and London: W. H. Freeman.
- HAMILTON, W. C. (1961). *Acta Cryst.* **14**, 185.
- HAMILTON, W. C. (1968). *Structural Chemistry and Molecular Biology*, Edited by A. RICH & N. DAVIDSON, p. 466. San Francisco and London: W. H. Freeman.
- HAMILTON, W. C. (1969). *Acta Cryst.* **A25**, 194.
- JOHNSON, C. K. (1965). ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- JONES, R. E. & TEMPLETON, D. H. (1958). *Acta Cryst.* **11**, 484.
- KANTERS, J. A., KROON, J., PEERDEMAN, A. F. & SCHOONE, J. C. (1967). *Tetrahedron*, **23**, 4027.
- NAHRINGBAUER, I. (1970). *Acta Chem. Scand.* **24**, 453.
- PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.
- RUDMAN, R. & GODEL, J. B. (1969). *J. Appl. Cryst.* **2**, 109.
- SCHUEURMAN, R. F. & SASS, R. L. (1962). *Acta Cryst.* **15**, 1244.
- SEQUEIRA, A., BERKEBILE, C. A. & HAMILTON, W. C. (1968). *J. Mol. Structure*, **1**, 283.
- STRIETER, F. J. & TEMPLETON, D. H. (1962). *Acta Cryst.* **15**, 1240.
- STRIETER, F. J., TEMPLETON, D. H., SCHUEURMAN, R. F. & SASS, R. L. (1962). *Acta Cryst.* **15**, 1233.

*Acta Cryst.* (1971). **B27**, 898

## Hydrogen-Bond Studies. XLV. The Crystal Structure of $\text{HClO}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$

BY JAN ALMLÖF, JAN-OLOF LUNDGREN AND IVAR OLOVSSON

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

(Received 1 June 1970)

The crystal structure of  $\text{HClO}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$  has been determined from three-dimensional single-crystal X-ray diffraction data recorded at  $-188^\circ\text{C}$ . The structure is monoclinic with space group  $P2_1/c$  and contains eight formula units. The cell dimensions are  $a=10\cdot960$ ,  $b=7\cdot132$ ,  $c=15\cdot167$  Å,  $\beta=124\cdot55^\circ$ . The structure contains  $\text{H}_2\text{O}$  molecules and  $\text{H}_3\text{O}^+$  ions interlinked by hydrogen bonds to form infinite helices. These helices form layers both by hydrogen bond interlinkage and by hydrogen bonding to the perchlorate ions. The two independent perchlorate ions show only minor deviations from tetrahedral symmetry, and the mean Cl-O distances are 1·435 and 1·439 Å.

### Introduction

This work is part of a systematic study of the hydrates of strong acids being carried out at this Institute aimed at investigating the hydration of the proton in the solid state. In  $\text{HBr} \cdot \text{H}_2\text{O}$  (Lundgren, 1970),  $\text{HCl} \cdot \text{H}_2\text{O}$  (Yoon & Carpenter, 1959),  $\text{HClO}_4 \cdot \text{H}_2\text{O}$  (Lee & Carpenter, 1959; Nordman, 1962),  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  (Taesler & Olovsson, 1968, 1969) the proton occurs as an  $\text{H}_3\text{O}^+$  ion, whereas  $\text{H}_5\text{O}_2^+$  has been found in  $\text{HCl} \cdot 2\text{H}_2\text{O}$  and  $\text{HCl} \cdot 3\text{H}_2\text{O}$  (Lundgren & Olovsson, 1967*a*, *b*),  $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$  (Olovsson, 1968),  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  (Kjällman & Olovsson, 1971), and in

$\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  (Williams & Peterson, 1969*a*). The investigations of  $\text{HClO}_4 \cdot 3\text{H}_2\text{O}$  (Almlöf, 1971) and  $\text{HBr} \cdot 4\text{H}_2\text{O}$  (Lundgren & Olovsson, 1968) have indicated the existence of  $\text{H}_7\text{O}_3^+$ . The latter compound has also been suggested to contain  $\text{H}_9\text{O}_4^+$  ions. The present investigation of  $\text{HClO}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$  is based on single-crystal X-ray diffraction data recorded at  $-188^\circ\text{C}$ .

### Experimental

A solution with the molar ratio  $\text{H}_2\text{O}:\text{HClO}_4=2\cdot50$  was prepared by diluting analytical grade perchloric acid (*ca.* 73%) with distilled water and analysed by titration