& Rollett is really significant, that a considerable strain in a bond angle may be tolerated if a more satisfactory packing or hydrogen bond pattern may be so achieved. The individual molecules in the crystal are held together by a three-dimensional network of hydrogen bonds in a manner which might well serve as a model to demonstrate the importance and effectiveness of such bond formation in determining the molecular packing within a crystal. The thoroughness and simplicity of the scheme may be seen from Fig. 3.

The two hydrogen atoms of the amino group both take part in bond formation, in the one case to form an intra-molecular linkage $N(1)\text{–}H\cdots O(1')$, in the other the bond $N(1)\text{–}H\cdots O(H_2O)$. In turn, the two hydrogens of the water molecule participate in the bonds $O(H_2O)\text{–}H\cdots O(2)$, $x, y-1, z$, and $O(H_2O)\text{–}H\cdots O(2)$, $\frac{1}{2}+x, \frac{1}{2}-y, \frac{3}{4}-z$ The lengths of these bonds, 2·83 and 2·75 Å, indicate that they are fairly weak interactions, and this is confirmed by the significantly higher value of B found for the water oxygen atoms than for the other light atoms.

The remaining hydrogen atom available for bond formation, that attached to N(3) bonds to O(1) of a neighbouring molecule, as shown. In turn, the atom N(3) of that molecule is involved in an analogous bond to the O(1) of the molecule one translation along a from the first, and so on, forming a spiralling system of interactions.

The sole van der Waals contacts between molecules occur at C(6) and N(3) where molecules approach to within 3·76 Å of each other.

We are indebted to the Computational Laboratories of the Massachusetts Institute of Technology and the Applied Physics Laboratory of Johns Hopkins University for the use of their facilities.

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The Crystal Structure of Acrylic Acid

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The structure of crystalline acrylic acid ($C_3H_4O_2$) has been determined at −135 °C by X-ray diffraction methods. The crystals were found to be orthorhombic, space group $Ibam\text{–}D_{2h}^{26}$ with 8 molecules per unit cell. The cell constants are

$$a=9\cdot966\pm0\cdot007,\ b=11\cdot744\pm0\cdot013,\ c=6\cdot306\pm0\cdot016\ \text{Å}\,.$$

The structure was refined by least-squares techniques. The molecules are planar hydrogen bonded dimers lying on crystallographic mirror planes.

Introduction

The structure of acrylic acid, ($CH_2=CH-COOH$), has been examined as part of a series of investigations of the structures of low molecular weight carboxylic acids. Acrylic acid is the simplest unsaturated aliphatic acid. Its melting point (12 °C) is some 30° higher than that of propionic acid (−22 °C) and very close to that of acetic acid (16·5 °C). This fact suggested that the hydrogen bonding system is of the infinite chain type as in acetic acid (Jones & Templeton, 1958) and not dimeric as in propionic acid (Strieter, Templeton, Scheerman & Sass, 1962). This investigation shows, however, that acrylic acid crystallizes in hydrogen bonded dimers across a symmetry center, the observed high melting point not being a consequence of the hydrogen bonding.

Experimental

Crystals of acrylic acid were obtained by partially freezing the pure 'Eastman grade' liquid in a tear bottle, pouring off the liquid phase and then cooling to −10 °C. Generally, several suitable crystals would be found projecting into the void left by the liquid. These were broken off and shaken onto an aluminum plate cooled by a block of dry ice. The crystals were then mounted in glass capillaries, carried to the X-ray machine on a piece of dry ice and placed in a goniometer head bathed in a stream of cold nitrogen gas. The temperature of the crystals was maintained at −35 °C during alignment and was then lowered to -115 ± 3 °C to record the diffraction data. No phase change was observed between the melting point and −115 °C. All diffraction patterns were obtained with Cu $K\alpha$ radiation on Kodak no-screen medical X-ray film. Oscillation and Weissenberg photographs show the crystals to be body-centered orthorhombic. The space group is either $Iba2(C_{2v}^{21})$ or $Ibam(D_{2h}^{26})$ derived from the following systematic absences:

hkl absent if $h+k+l=2n+1$
$0kl$ absent if $k=2n+1$
$h0l$ absent if $h=2n+1$
($hk0$ absent if $h+k=2n+1$).

The cell constants a and b were determined from a zero layer Weissenberg photograph which was calibrated with a superimposed NaCl (a_0 = 5·637 Å) powder pattern. The c axis was determined from a rotation photograph calibrated by a superimposed NaCl rotation diffraction pattern. The following values were obtained:

$$a = 9\cdot966 \pm 0\cdot007,\ b = 11\cdot744 \pm 0\cdot013,$$
$$c = 6\cdot306 \pm 0\cdot016\ \text{Å}\,.$$

These constants, assuming eight molecules/unit cell, result in a calculated density for solid acrylic acid of 1·296 g.cm^{-3}. There has been no experimental density determination made on solid acrylic acid, but density of the liquid at 12 °C has been reported to be 1·0600 g.cm^{-3} (Moureau & Boutaric, 1920).

Treatment of data

Weissenberg photographs of the $l=0$, 1, 2 and 3 layers were taken with sets of four films and the intensities were estimated visually, a standard intensity strip being employed. The various layers were correlated by comparison with a photograph which contained 15-minute exposures of a 25 degree portion of each layer. The intensities were corrected with the proper Lorentz, polarization and Tunnell factors. No correction for absorption was deemed necessary since μr was calculated to be 0·148.

If the correct space group is the centric *Ibam*, the molecules must be in the special positions

$$8(j):\ (000,\ \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}) + xy0,\ \bar{x}\bar{y}0,\ \bar{x}y\tfrac{1}{2},\ x\bar{y}\tfrac{1}{2}\,.$$

Under these restrictions, the calculated unitary structure factors of constant h and k values should be equal for all values of l of the same parity. For particular values of h and k then, $F_{hk0}/\hat{f}_{hk0} = F_{hk2}/\hat{f}_{hk2}$ where $\hat{f}$ is the unitary form factor. Taking $\hat{f} = \frac{1}{2}(\frac{1}{8}f_o + \frac{1}{6}f_c)$, a plot of $F_{hk0}/\hat{f}_{hk0}$ *vs.* $F_{hk2}/\hat{f}_{hk2}$ for 25 random pairs of reflections is shown in Fig. 1. The data for this plot are on an arbitrary scale and no correction was made for the effects of thermal vibration. The fact that the plotted points fall close to a straight line influenced us to assume that the centric space group is the correct one.

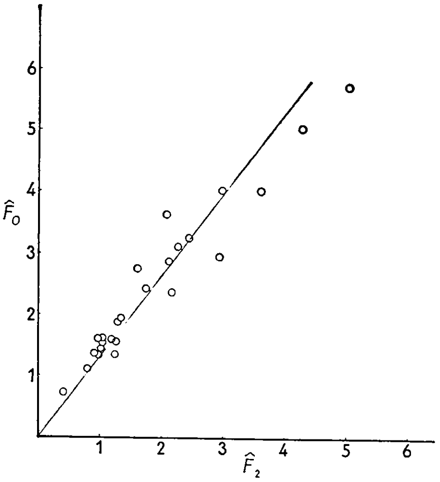

Fig. 1. A plot of $F_{hk0}/\hat{f}_{hk0}$ versus $F_{hk2}/\hat{f}_{hk2}$ for 25 pairs of reflections.

An attempt was made to determine a correct trial structure from the Patterson projection $P(uv)$. The resulting map was poorly resolved and several attempts failed to lead to a solution. Because the atoms are in special positions, it is possible effectively to subtract out the body centered molecules and reduce the problem to that of a primitive cell. In the space group *Ibam* with molecules in position $8(j)$, the structure factors of the $l=0$ and $l=1$ layer are respectively

$$F_{hk0} = 8\Sigma_j f_j(\cos 2\pi hx_j)(\cos 2\pi ky_j)\,;\ (h+k=2n)$$
$$F_{hk1} = -8\Sigma_j f_j(\sin 2\pi hx_j)(\sin 2\pi ky_j)\,;\ (h+k=2n+1).$$

In the primitive space group *Pbam*, the special position $4g$ are related to positions $8(j)$ of *Ibam* by removing the body centering condition. The corresponding expression for the $l=0$ structure factors are

$$F_{hk0} = 4\Sigma_j f_j(\cos 2\pi hx_j)(\cos 2\pi hy_j)\,;\ (h+k=2n)$$
$$F_{hk0} = -4\Sigma_j f_j(\sin 2\pi hx_j)(\sin 2\pi ky_j)\,;\ (h+k=2n+1).$$

Thus by multiplying the observed values of F_{hk1} by the ratio of unitary form factors $\hat{f}_{hk0}/\hat{f}_{hk1}$, the combined zero and first layer data can be used to calculate the Patterson projection for the primitive cell. It is obvious that this process is quite closely related to calculating the $w=0$ Patterson section of the body-centered cell but requires the use of much fewer data. This synthesis was well resolved and led immediately to a trial structure consisting of hydrogen-bonded dimers across a center of symmetry. Only the five 'heavy' atoms were located. The trial structure was refined by a least-squares treatment of the $l=0$, 1 and 2 layer data. A total of 119 observed and 51 unobserved (too weak) reflections were used in the calculation. The unobserved reflections were given a value of one-half the minimum observable value. These calculations were carried out on the Rice Computer (Rice University, 1962) with a program written for that machine. The diagonal approximation of the normal equation matrix was used. All non-diagonal elements were set to zero. Several iterations were first carried out on only the positional parameters. The thermal vibration parameters were allowed to vary during the final cycles of refinement. After

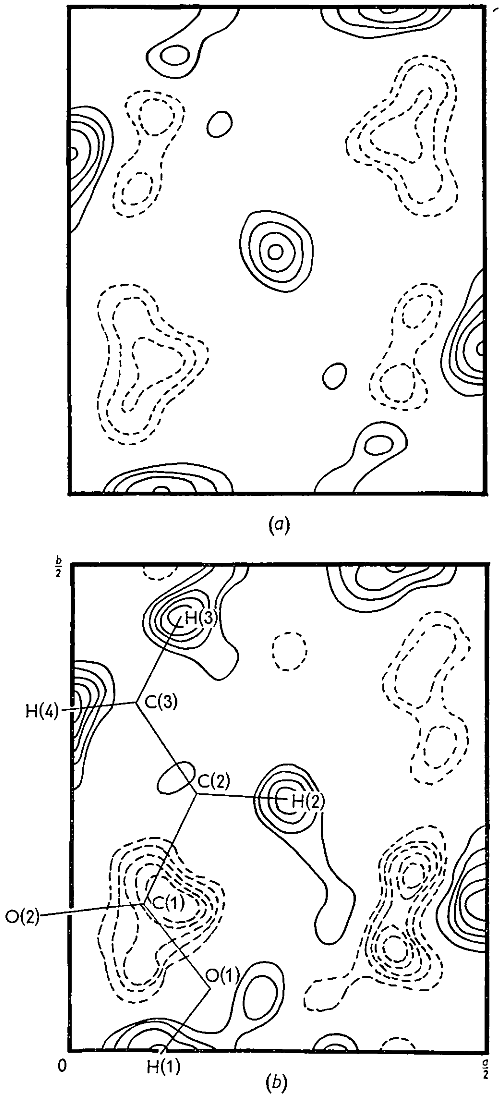

Fig. 2. $\varrho(xy)_o - \varrho(xy)_c$: (a) centered cell; (b) primitive cell.

Table 1. *Acrylic acid: Final values of F_c and F_o including hydrogen atom contributions*

h k 0				h k 1				h k 2			
h	k	F_c	$\lvert F_o\rvert$	h	k	F_c	$\lvert F_o\rvert$	h	k	F_c	$\lvert F_o\rvert$
0	2	-3.68	3.45	1	2	-1.66	1.82	0	2	-2.22	2.16
0	4	-7.75	6.74	1	4	-4.90	5.47	0	4	-5.70	5.90
0	6	0.18	<0.36	1	6	-1.63	2.05	0	6	0.14	<0.24
0	8	1.95	2.20	1	8	-0.39	<0.37	0	8	1.62	2.18
0	10	-4.09	4.17	1	10	1.49	1.53	0	10	-3.44	4.17
1	1	7.59	6.39	2	1	-9.81	10.54	1	1	5.70	5.95
1	3	-2.61	2.51	2	3	-2.08	2.09	1	3	-2.16	2.19
1	5	-2.85	2.77	2	5	-2.99	3.63	1	5	-2.19	1.41
1	7	1.81	1.66	2	7	-0.33	<0.34	1	7	1.46	1.53
1	9	-0.94	0.89	2	9	-0.85	0.61	1	9	-0.80	0.71
1	11	-0.74	0.52	2	11	1.92	1.96	1	11	-0.63	0.83
2	0	6.50	5.62	3	2	3.38	4.28	2	0	4.50	5.00
2	2	-2.48	2.58	3	4	-0.30	<0.27	2	2	-1.91	1.64
2	4	-8.39	7.66	3	6	-1.39	1.41	2	4	-6.12	6.50
2	6	4.82	4.68	3	8	0.27	<0.38	2	6	3.71	3.62
2	8	2.69	2.88	3	10	0.75	0.56	2	8	2.16	2.36
2	10	-0.97	1.10	4	1	2.13	2.10	2	10	-0.82	0.84
3	1	2.96	2.86	4	3	2.20	2.35	3	1	-2.17	1.76
3	3	-4.73	4.76	4	5	3.80	4.23	3	3	-3.58	3.43
3	5	0.92	0.89	4	7	-0.85	0.83	3	5	0.73	0.51
3	7	2.70	2.74	4	9	-0.38	<0.41	3	7	2.13	2.13
3	9	1.94	1.83	4	11	-0.07	<0.39	3	9	1.61	1.48
3	11	-0.63	0.71	5	2	4.97	4.70	3	11	-0.54	0.65
4	0	-5.37	4.34	5	4	1.85	1.97	4	0	-3.88	3.18
4	2	-0.08	<0.32	5	6	-1.11	1.15	4	2	0.04	<0.23
4	4	1.92	2.29	5	8	0.96	0.95	4	4	-1.45	1.63
4	6	1.51	1.58	5	10	-0.24	<0.41	4	6	1.18	1.02
4	8	0.52	0.81	6	1	2.96	2.97	4	8	0.37	<0.30
4	10	1.03	0.96	6	3	0.46	<0.36	4	10	0.90	0.77
5	1	1.93	1.91	6	5	-0.72	<0.38	5	1	1.46	1.27
5	3	0.13	<0.38	6	7	-0.78	0.86	5	3	0.15	<0.27
5	5	-0.91	1.15	6	9	0.94	0.92	5	5	-0.71	0.78
5	7	-0.68	0.88	7	2	1.01	0.69	5	7	-0.57	0.47
5	9	-0.17	<0.51	7	4	-2.01	1.75	5	9	-0.13	<0.35
5	11	-0.19	<0.47	7	6	-1.81	1.86	5	11	-0.15	<0.30
6	0	0.80	2.17	7	8	0.59	0.58	6	0	0.59	<0.29
6	2	1.56	1.53	7	10	0.76	0.91	6	2	1.22	1.03
6	4	2.87	2.51	8	1	0.81	0.74	6	4	2.41	1.96
6	6	-3.29	2.97	8	3	0.83	0.83	6	6	-2.77	2.36
6	8	-1.15	1.29	8	5	-3.43	3.37	6	8	-0.97	0.97
6	10	0.28	<0.53	8	7	0.24	<0.40	6	10	0.26	<0.31
7	1	0.66	0.62	8	9	0.94	0.86	7	1	0.52	0.40
7	3	0.90	1.14	9	2	0.94	0.96	7	3	0.75	0.64
7	5	-0.56	0.64	9	4	-0.48	<0.41	7	5	-0.47	0.50
7	7	-0.35	<0.50	9	6	-0.36	<0.39	7	7	-0.30	<0.34
7	9	-0.53	<0.49	9	8	0.18	<0.34	7	9	-0.45	<0.31
7	11	0.25	<0.38	9	10	0.32	<0.51	7	11	0.23	<0.23
8	0	1.93	1.81	10	1	1.33	1.31	8	0	-1.61	1.07
8	2	-0.32	<0.50	10	3	1.03	0.72	8	2	-0.26	<0.35
8	4	1.63	1.75	10	5	-0.69	<0.36	8	4	1.38	1.30
8	6	-0.65	0.78	10	7	0.20	<0.30	8	6	-0.57	<0.33
8	8	-0.06	<0.41	10	9	0.49	<0.19	8	8	-0.05	<0.30
8	10	0.55	<0.39					8	10	0.49	<0.23
9	1	-1.12	1.31					9	1	-0.92	0.77
9	3	-0.22	<0.17					9	3	-0.20	<0.33
9	5	0.62	<0.50					9	5	0.53	0.45
9	7	0.30	<0.46					9	7	0.26	<0.29
9	9	0.37	<0.32					9	9	0.32	<0.22
10	0	-1.12	1.52					10	0	-0.95	0.75

convergence had been obtained, several additional cycles were run during which the positional parameters oscillated around the reported values by no more than ±0·0001 (fractional part of cell dimension) and the thermal vibration parameters oscillated by less than ±0·01 Å². The weighting scheme used was

$$w = 1/|F_o| \text{ if } |F_o| > 4|F_{\min}|$$
$$w = 1/4|F_{\min}| \text{ if } |F_o| < |F_{\min}| .$$

Individual isotropic temperature factors were refined for all atoms. The carbon and oxygen form factors were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955). The form factors were stored in a table of 64 entries for equally spaced values of sin θ/λ from 0 to 1; linear interpolation was used. During refinement the value of R (observed reflections only) was reduced to 13·0. At this point electron density difference syntheses were calculated to locate the hydrogen atoms. The calculated structure factors used were those of the final cycle of least squares including only the heavy atoms. The projections ($\varrho_o - \varrho_c$) down the c axis are shown in Fig. 2 for the body centered and primitive structure. The contours start at 0·2 electrons/Å² and are at intervals of 0·2 electrons in the body centered structure and at intervals of 0·1 electrons in the primitive structure. In the body centered cell three of the four hydrogen atoms overlap with equivalent hydrogen atoms from adjacent molecules. In the primitive structure all hydrogen atoms are resolved. The coordinates of the various hydrogen atoms were measured, included in the calculated structure factors and the heavy atom positions were further refined. The final value of R including hydrogen atoms is 10·2. The form factor used by hydrogen was that of McWeeny (1951). The final calculated and observed structure factors are listed in Table 1. (These values are reduced by a factor of 8.) The final values of the atomic parameters are listed in Table 2. The estimated standard deviations reported in this table were obtained from the least-squares treatment.

Table 2. *Acrylic acid: Final values of atomic parameters*

	x	y	z	B	$\sigma(x)$	$\sigma(y)$
O(1)	0·1655	0·0635	0	4·33	0·0007	0·0006
O(2)	−0·0402	0·1362	0	4·42	0·0007	0·0006
C(1)	0·0854	0·1487	0	3·49	0·0009	0·0008
C(2)	0·1492	0·2615	0	4·33	0·0010	0·0009
C(3)	0·0765	0·3538	0	4·63	0·0010	0·0009
H(1)	0·113	−0·004	0	4·5*		
H(2)	0·256	0·258	0	4·5*		
H(3)	0·130	0·442	0	4·5*		
H(4)	−0·014	0·347	0	4·5*		

* Assumed values.

Discussion of the structure

Acrylic acid crystallizes as planar, hydrogen bonded dimers. The arrangement of a single layer of molecules in the $z=0$ plane is shown in Fig. 3. Bond distances and angles are presented in Table 3. Within experimental error, the C–C double bond is of expected length and the C–C single-bond length is that of a normal sp^2–sp^2 bond. The C=O bond length is somewhat longer and the C–O bond length is shorter than the corresponding values observed in normal saturated carboxylic acids, but they agree well with observed distances in unsaturated and aromatic acids. All bond angles are normal. A representative listing of carboxylic acids is presented in Table 4. With the exception of 2-naphthoic acid, the carboxyl group dimensions fall into two classes. In the saturated dimeric acids the two C–O bonds lengths differ by approximately 0·11 Å. These two distances in the unsaturated acids are, however, very nearly the same, differing by only 0·03 Å on the average. It is of interest that although the dimeric gas phase formic and acetic acid dimensions are consistent with crystalline dimeric propionic, butyric and valeric acids, the crystalline forms of formic and acetic acids, which consist of infinite hydrogen bonded chains,

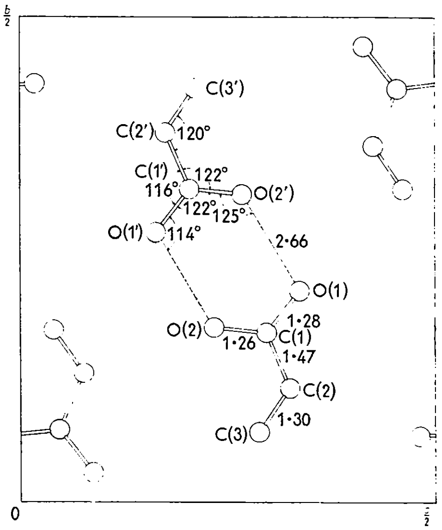

Fig. 3. Molecular configuration and dimensions in the $z=0$ plane.

Table 3. *Acrylic acid: Bond lengths and angles*

Bond	Length ± e.s.d.	Angle	
C(1)–C(2)	1·47 ± 0·015 Å	C(2)–C(1)–O(2)	122 ± 1°
C(2)–C(3)	1·30 ± 0·015	C(2)–C(1)–O(1)	116 ± 1
C(1)–O(1)	1·28 ± 0·014	O(1)–C(1)–O(2)	122 ± 1
C(1)–O(2)	1·26 ± 0·014	C(1)–O(1)–H(1)	111
O(1)–H(1)	0·95 ± 0·1	C(1)–O(1) · · · O(2)	114 ± 1
C(2)–H(2)	1·06 ± 0·1	C(1)–O(2) · · · O(1′)	125 ± 1
C(3)–H(3)	1·16 ± 0·1	C(1)–C(2)–H(2)	114
C(3)–H(4)	0·91 ± 0·1	C(3)–C(2)–H(2)	126
O(1) · · · O(2′)	2·66 ± 0·014	C(1)–C(2)–C(3)	120 ± 1
		C(2)–C(3)–H(4)	129
		C(2)–C(3)–H(3)	119
		H(3)–C(3)–H(4)	112

Table 4. *Bond distances and angles in various carboxylic acids*

Compound	C–OH	C=O	R–C–OH	R–C–O	O=C–OH	O···O	Compound type	Reference
Formic acid	1·36 Å	1·25 Å			121°	2·73 Å	Gas, dimer	Karle & Brockway (1944)
Acetic acid	1·36	1·25	110°	120°	130	2·76	Gas, dimer	Karle & Brockway (1944)
Propionic acid	1·33	1·22	113	125	122	2·64	Crystal, dimer	Strieter, Templeton, Scheuerman & Sass (1962)
Butyric acid	1·34	1·22	114_5	126	119_5	2·66	Crystal, dimer	Strieter & Templeton (1962)
Valeric acid	1·35	1·26	116_5	125	118_5	2·63	Crystal, dimer	Scheuerman & Sass (1962)
Average	1·35 Å	1·24 Å	114°	124°	122°			
Acetylene dicarboxylic acid	1·27 Å	1·26 Å	117°	123°	120°		Crystal, dimer	Dumitz & Robertson (1947)
Acrylic acid	1·28	1·26	116	122	122	2·66	Crystal, dimer	This paper
Benzoic acid	1·29	1·24	118	122	122	2·64	Crystal, dimer	Sim, Robertson & Goodwin (1955)
Formic acid	1·26	1·23		123		2·58	Crystal, infinite chain	Holtzberg, Post & Fankucken (1953)
Acetic acid	1·29	1·24	116	122	122	2·61	Crystal, infinite chain	Jones & Templeton (1958)
1-Naphthoic acid	1·28	1·25	122	127	110	2·58	Crystal, dimer	Trotter (1960)
2-Naphthoic acid	1·37	1·33	127	122	112	2·54	Crystal, dimer	Trotter (1961)

contain C–O distances very similar to those of the unsaturated acids.

The various bonded hydrogen distances are probably accurate to only about ±0·1 Å. The average C–H distance of 1·04 Å is fortuitously close to the accepted value of 1·07 Å. The measured value of 0·95 Å for the O–H distance leaves no doubt that the hydrogen atom is singly bonded and not symmetrical in the hydrogen bond as might be implied from the similarity of the two C–O distances.

All heavy atom intramolecular contact distances less than or equal to 3·50 Å are, in the same plane

O(1)–O(2)	2·66 Å	(hydrogen bond)
C(2)–O(2)	3·32 Å	

between planes

C(3)–C(3″)	3·50 Å
C(1)–O(2″)	3·19 Å
O(1)–O(2″)	3·49 Å .

Note added October 23, 1962: It has recently come to the attention of the authors that a paper discussing the structure of acrylic acid was presented by Isamu Nitta at the Cambridge meeting of the International Union of Crystallography in 1960. The paper is abstracted in *Acta Cryst.* (1960), **13**, 1035. The gross structure there presented is the same as found in the present paper, but the bond distances reported for the carboxyl group are significantly different. So far as the authors know, no further account of this work has been published.

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