

The Crystal Structure of Propionic Acid*

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The structure of propionic acid crystals has been determined in two independent investigations of single crystals by X-ray diffraction. The crystals are monoclinic, space group $P2_1/c$. The unit cell dimensions according to one study at -95°C . are

$$a = 4.04 \pm 0.04, b = 9.06 \pm 0.01, c = 11.00 \pm 0.01 \text{ \AA}; \beta = 91^\circ 15' \pm 8'.$$

According to the other work at -135°C .,

$$a = 4.07 \pm 0.01, b = 9.04 \pm 0.01, c = 10.97 \pm 0.01 \text{ \AA}; \beta = 90^\circ 56' \pm 8'.$$

Atomic coordinates were refined in each case by least-squares methods to give substantially the same structure. Propionic acid molecules occur in the crystal as centric and nearly planar dimers with hydrogen bonds of length 2.64 Å. Other bond lengths are: C–O, 1.23 and 1.32 Å; C–C(α), 1.50 Å; C–C(β), 1.54 Å, all with standard deviations of about 0.01 Å.

Introduction

The crystal structures of the normal fatty acids of low molecular weight have been rather neglected until recently. Formic acid (Holtzberg, Post & Fankuchen, 1953) and acetic acid (Jones & Templeton, 1958) occur in the solid as hydrogen-bonded linear polymers, while several acids with eleven or more carbon atoms per molecule exist in the solid as dimers (Vand, Morley & Lomer, 1951; von Sydow, 1956). The melting points of these acids, when plotted against number of carbon atoms, fall on two rather similar curves for even and odd numbers of carbon atoms, respectively, each with a minimum near five carbon atoms. These facts and hope of explaining the melting-point behavior led us in two independent groups to examine the structures of other fatty acids. Propionic and butyric acids were investigated (by Strieter & Templeton) at Berkeley (Strieter, 1959). Propionic and valeric acids were studied at Houston (by Scheuerman & Sass), and a preliminary study of butyric acid was also done there. This paper describes the two independent determinations of the structure of propionic acid. The two determinations present an interesting comparison because the details are different in several respects, but the results are in substantial agreement. The

structures of butyric and valeric acid will be described elsewhere. All three of these acids occur in the crystals as dimers.

Determination of the structure at Berkeley

Experimental procedure

Propionic acid ($\text{CH}_3\text{CH}_2\text{COOH}$) was studied with a modified Weissenberg camera (Olovsson & Templeton, 1959) in which a stream of cold nitrogen gas was directed over the capillary containing the sample. Temperatures were measured with a copper-constantan thermocouple placed in the cooling stream 0.5 cm. from the end of the capillary. The melting point of the propionic acid sample was determined with this thermocouple as -20.5° , in good agreement with the reported value of -20.7° (Timmermans, 1952). A cylindrical single crystal, 5 mm. long and 0.3 mm. in diameter, was grown for us by Dr I. Olovsson. Rotation and multiple-film Weissenberg photographs were taken at $-95^\circ \pm 2^\circ$ with Cu K radiation, in some cases filtered with Ni. Unit cell dimensions were obtained from the uncalibrated rotation photo-

Table 1. *Unit cell dimensions of propionic acid*

	Strieter & Templeton	Scheuerman & Sass
	-95°C .	-135°C .
<i>a</i>	$4.04 \pm 0.04 \text{ \AA}$	$4.07 \pm 0.01 \text{ \AA}$
<i>b</i>	9.06 ± 0.01	9.04 ± 0.01
<i>c</i>	11.00 ± 0.01	10.97 ± 0.01
β	$91^\circ 15' \pm 8'$	$90^\circ 56' \pm 8'$

* Work at Berkeley done under the auspices of the U.S. Atomic Energy Commission; work at Houston done under the auspices of the National Aeronautic and Space Administration.

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Table 2 (cont.)

S & T.				S & S.				S & T.				S & S.				S & T.				S & S.														
h	k	l	$ F_0 $	F_c	$ F_0 $	F_c	h	k	l	$ F_0 $	F_c	$ F_0 $	F_c	h	k	l	$ F_0 $	F_c	$ F_0 $	F_c	h	k	l	$ F_0 $	F_c	$ F_0 $	F_c	h	k	l	$ F_0 $	F_c	$ F_0 $	F_c
1	7	7	2.2	-1.1	1.31*	-1.81	2	2	-7	6.9	-5.9	5.99	-5.89	2	6	0	2.7	-2.3	1.88*	-1.13	2	6	0	2.7	-2.3	1.88*	-1.13	2	6	0	2.7	-2.3		
1	7	8	6.1	5.8	5.35	4.76	2	2	6	5.1	-3.0	3.49	-3.75	2	6	1	1.0*	0.7	1.88*	0.16	2	6	1	1.0*	0.7	1.88*	0.16	2	6	1	1.0*	0.7		
1	7	9	2.5	2.4	2.38	2.28	2	2	-5	0.8*	-0.3	1.60*	-0.77	2	6	2	15.7	14.5	12.93	13.21	2	6	2	15.7	14.5	12.93	13.21	2	6	2	15.7	14.5		
1	7	10	3.1	2.5	2.77	2.16	2	2	4	13.5	14.5	12.45	14.02	2	6	3	13.2	14.0	11.31	12.10	2	6	3	13.2	14.0	11.31	12.10	2	6	3	13.2	14.0		
1	7	11	0.3*	-0.1			2	2	-3	29.4	29.5	26.67	27.88	2	6	4	2.1	-2.5	1.98*	-1.90	2	6	4	2.1	-2.5	1.98*	-1.90	2	6	4	2.1	-2.5		
1	8	9	1.0*	0.9			2	2	-2	1.5	1.1	1.13*	0.77	2	6	5	3.0	1.6			2	6	5	3.0	1.6			2	6	5	3.0	1.6		
1	8	10	4.7	4.2	3.63	3.72	2	2	-1	4.3	-2.5	3.33	-3.43	2	6	6	4.4	-3.5			2	6	6	4.4	-3.5			2	6	6	4.4	-3.5		
1	8	11	4.1	4.0	3.77	3.52	2	2	0	14.3	-17.4	14.44	-14.80	2	6	7	2.8	2.7			2	6	7	2.8	2.7			2	6	7	2.8	2.7		
1	8	12	3.6	3.2	3.40	2.64	2	2	1	5.6	-6.1	4.11	-6.55	2	6	8	3.5	-2.7			2	6	8	3.5	-2.7			2	6	8	3.5	-2.7		
1	8	13	2.2	-2.5	1.77*	-1.72	2	2	2	19.4	-21.8	18.42	-22.36	2	6	9	0.8*	-0.5			2	6	9	0.8*	-0.5			2	6	9	0.8*	-0.5		
1	8	14	1.6*	-1.3	1.80*	-1.53	2	2	3	5.9	-5.2	4.77	-5.12	2	6	10	0.6*	0.9			2	6	10	0.6*	0.9			2	6	10	0.6*	0.9		
1	8	15	5.0	-4.7	3.97	-3.63	2	2	4	15.2	14.3	15.90	14.08	2	7	-9	0.6*	0.5			2	7	-9	0.6*	0.5			2	7	-9	0.6*	0.5		
1	8	16	2.3	-1.0	1.83*	-0.91	2	2	5	0.9*	1.0	1.19*	0.14	2	7	-8	2.5	1.6			2	7	-8	2.5	1.6			2	7	-8	2.5	1.6		
1	8	17	6.2	4.9	5.22	5.01	2	2	6	6.5	5.9	6.75	5.39	2	7	-7	0.9*	1.1			2	7	-7	0.9*	1.1			2	7	-7	0.9*	1.1		
1	8	18	3.4	-2.8	2.69	-1.92	2	2	7	9.6	-10.3	11.30	-9.63	2	7	-6	3.3	-3.0	2.65	-2.43	2	7	-6	3.3	-3.0	2.65	-2.43	2	7	-6	3.3	-3.0		
1	8	19	6.2	5.3	4.88	4.47	2	2	8	1.5	-1.0	1.46*	-1.31	2	7	-5	1.0*	-0.1	1.93*	-0.57	2	7	-5	1.0*	-0.1	1.93*	-0.57	2	7	-5	1.0*	-0.1		
1	8	20	7.3	-7.5	6.55	-7.12	2	2	9	4.8	4.7	5.42	3.94	2	7	-4	1.0*	0.2	1.98*	0.47	2	7	-4	1.0*	0.2	1.98*	0.47	2	7	-4	1.0*	0.2		
1	8	21	7.1	5.7	5.89	-5.63	2	2	10	2.9	-2.1	3.10	-1.72	2	7	-3	1.0	0.3	1.98*	0.20	2	7	-3	1.0	0.3	1.98*	0.20	2	7	-3	1.0	0.3		
1	8	22	4.0*	0.2	1.35*	-0.24	2	2	11	4.2	3.3	4.56	2.75	2	7	-2	10.1	10.6	9.28	9.72	2	7	-2	10.1	10.6	9.28	9.72	2	7	-2	10.1	10.6		
1	8	23	5.2	-3.9	4.27	-4.00	2	2	12	5.3	4.7	6.37	4.10	2	7	-1	1.0*	0.7	1.98*	1.54	2	7	-1	1.0*	0.7	1.98*	1.54	2	7	-1	1.0*	0.7		
1	8	24	4.6	4.3	4.52	3.97	2	3	-12	1.8	1.7			2	7	0	7.0	6.3	5.02	6.06	2	7	0	7.0	6.3	5.02	6.06	2	7	0	7.0	6.3		
1	8	25	2.6	3.3	2.28	2.64	2	3	-11	1.6	2.1			2	7	1	2.1	-3.2	1.98*	-2.46	2	7	1	2.1	-3.2	1.98*	-2.46	2	7	1	2.1	-3.2		
1	8	26	3.9	3.5	3.48	2.97	2	3	-10	2.9	2.9			2	7	2	11.9	-12.0	9.62	-10.73	2	7	2	11.9	-12.0	9.62	-10.73	2	7	2	11.9	-12.0		
1	8	27	2.6	1.9	2.67	1.69	2	3	-9	1.0*	-0.5			2	7	3	1.1*	-1.8	1.98*	-1.48	2	7	3	1.1*	-1.8	1.98*	-1.48	2	7	3	1.1*	-1.8		
1	9	-8	4.9	4.3	4.09	3.46	2	3	-8	2.0*	-0.6			2	7	4	5.5	-5.1	4.41	-4.85	2	7	4	5.5	-5.1	4.41	-4.85	2	7	4	5.5	-5.1		
1	9	-7	6.2	4.6	4.24	3.53	2	3	-7	1.4	1.3			2	7	5	2.9	1.9			2	7	5	2.9	1.9			2	7	5	2.9	1.9		
1	9	-6	1.2*	1.1	1.41*	1.10	2	3	-6	2.1	-2.0			2	7	6	2.0	2.1			2	7	6	2.0	2.1			2	7	6	2.0	2.1		
1	9	-5	2.3	-2.8	1.56*	-1.39	2	3	-5	10.0	10.1	9.11	11.14	2	7	7	1.6	1.8			2	7	7	1.6	1.8			2	7	7	1.6	1.8		
1	9	-4	3.0	2.9	2.73	2.40	2	3	-4	1.1	-2.0	1.59*	-2.01	2	7	8	2.0	1.5			2	7	8	2.0	1.5			2	7	8	2.0	1.5		
1	9	-3	1.5*	0.5	1.73*	0.32	2	3	-3	5.3	5.6	4.35	5.50	2	7	9	1.9	-1.2			2	7	9	1.9	-1.2			2	7	9	1.9	-1.2		
1	9	-2	9.9	-10.1	9.21	-8.94	2	3	-2	1.7	-2.2	1.33*	-2.00	2	8	-8	4.2	3.8	2.97	2.64	2	8	-8	4.2	3.8	2.97	2.64	2	8	-8	4.2	3.8		
1	9	-1	1.5*	-0.4	1.77*	-1.30	2	3	-1	11.0	-11.5	9.23	-13.00	2	8	-7	3.4	3.4	2.09	2.32	2	8	-7	3.4	3.4	2.09	2.32	2	8	-7	3.4	3.4		
1	9	0	10.3	9.6	8.73	8.78	2	3	0	1.9	0.5	1.26*	0.19	2	8	-6	0.8*	-0.6	1.60*	-0.00	2	8	-6	0.8*	-0.6	1.60*	-0.00	2	8	-6	0.8*	-0.6		
1	9	1	2.6	-1.1	2.04	-1.78	2	3	1	18.7	-20.5	17.87	-20.73	2	8	-5	3.1	-4.1	3.94	-3.28	2	8	-5	3.1	-4.1	3.94	-3.28	2	8	-5	3.1	-4.1		
1	9	2	3.0	2.9	2.73	2.40	2	3	2	5.0	3.5	3.81	2.61	2	8	-4	5.1	5.7	4.41	4.95	2	8	-4	5.1	5.7	4.41	4.95	2	8	-4	5.1	5.7		
1	9	3	5.4	-5.3	4.66	-3.74	2	3	3	0.8*	0.9	1.08*	0.92	2	8	-3	1.0	-2.0	1.91*	-1.17	2	8	-3	1.0	-2.0	1.91*	-1.17	2	8	-3	1.0	-2.0		
1	9	4	2.9	-2.3	2.29	-2.44	2	3	4	2.4*	-0.8	1.69	-2.03	2	8	-2	5.1	-4.4	3.91	-4.16	2	8	-2	5.1	-4.4	3.91	-4.16	2	8	-2	5.1	-4.4		
1	9	5	4.1	4.2	3.58	3.09	2	3	5	5.2	4.5	5.06	4.35	2	8	-1	7.8	7.5	7.27	7.24	2	8	-1	7.8	7.5	7.27	7.24	2	8	-1	7.8	7.5		
1	9	6	1.1	-1.2			2	3	6	2.8	2.8	2.86	2.49	2	8	0	2.5	-2.1	1.96*	-1.33	2	8	0	2.5	-2.1	1.96*	-1.33	2	8	0	2.5	-2.1		
1	9	7	1.4	1.5			2	3	7	2.8	2.8	2.78	2.29	2	8	1	2.8	2.0	1.96*	1.00	2	8	1	2.8	2.0	1.96*	1.00	2	8	1	2.8	2.0		
1	9	8	6.1	6.5			2	3	8	2.8	2.6	3.33	2.55	2	8	2	6.5	-6.6	4.32	-5.08	2	8	2	6.5	-6.6	4.32	-5.08	2	8	2	6.5	-6.6		
1	10	-6	0.9*	0.7			2	3	9	1.0*	-0.6	1.44*	-0.33	2	8	3	9.0	-9.7	8.00	-8.49	2	8	3	9.0	-9.7	8.00	-8.49	2	8	3	9.0	-9.7		
1	10	-5	6.1	-4.3	4.41	-3.97	2	3	10	1.9	-0.4	1.36*	-0.68	2	8	4	3.9	3.5			2	8	4	3.9	3.5			2	8	4	3.9	3.5		
1	10	-4	1.1*	-1.4	1.34*	-1.31	2	3	11	3.1	2.7	3.76	2.40	2	8	5	3.9*	0.7			2	8	5	3.9*	0.7			2	8	5	3.9*	0.7		
1	10	-3	5.3	-3.5	3.83	-3.11	2	3	12	3.6	-3.4	4.44	-2.79	2	8	6	0.8*	0.7			2	8	6	0.8*	0.7			2	8	6	0.8*	0.7		
1	10	-2	2.2	1.8	1.96	1.26	2	4	-12	3.2	4.4			2	8	7	8	7	5.4	5.7	2	8	7	8	7	5.4	5.7	2	8	7	8	7	5.4	5.7
1	10	-1	1.3	1.2	1.52*	1.07	2	4	-11	3.6	3.5	2.19	3.25	2	8	8	3.7	3.0			2	8	8	3.7	3.0			2	8	8	3.7	3.0		
1	10	0	1.5	1.9	1.52	1.36	2	4	-10	1.7	-0.9	1.69*	-0.46	2	9	-6	4.6	-4.1	3.13	-3.51	2	9	-6	4.6	-4.1	3.13	-3.51	2	9	-6	4.6	-4.1		
1	10	1	1.7	1.2			2	4	-9	8.6	10.3	7.84	9.17	2	9	-5	0.7*	-0.6	1.43*	-0.41	2	9	-5	0.7*	-0.6	1.43*	-0.41	2	9	-5	0.7*	-0.6		
1	10	2	0.8*	0.6			2	4	-8	5.8	-6.																							

Table 2 (cont.)

S. & T.					S. & T.					S. & T.					S. & T.				
h	k	l	$ F_0 $	F_c	h	k	l	$ F_0 $	F_c	h	k	l	$ F_0 $	F_c	h	k	l	$ F_0 $	F_c
3	1	11	3.6	3.8	3	3	1	7.2	-7.3	3	5	-6	0.9*	1.2	3	7	-7	1.1	0.9
3	2	-11	0.6*	0.3	3	3	2	7.0	-6.1	3	5	-5	1.0*	-0.4	3	7	-6	4.2	4.1
3	2	-10	0.8	-1.9	3	3	3	4.8	4.0	3	5	-4	1.0*	-0.5	3	7	-5	2.3	3.7
3	2	-9	4.2	5.1	3	3	4	6.0	-5.6	3	5	-3	4.1	-3.8	3	7	-4	4.3	-4.6
3	2	-8	1.7	-1.5	3	3	5	5.6	-4.3	3	5	-2	2.6	-1.9	3	7	-3	3.4	-2.5
3	2	-7	1.4	1.2	3	3	6	2.8	2.1	3	5	-1	4.1	-4.0	3	7	-2	4.6	-4.9
3	2	-6	6.4	8.3	3	3	7	3.4	3.4	3	5	0	8.9	-8.2	3	7	-1	1.9	-2.2
3	2	-5	6.9	-7.0	3	3	8	2.0	1.3	3	5	1	14.2	14.7	3	7	0	4.0	-3.3
3	2	-4	5.6	6.4	3	3	9	2.1	1.7	3	5	2	1.0*	-1.1	3	7	1	2.7	1.3
3	2	-3	1.1	-2.3	3	3	10	2.4	-2.2	3	5	3	1.0*	0.8	3	7	2	8.5	9.5
3	2	-2	7.5	-7.5	3	4	-10	3.2	-3.2	3	5	4	5.0	-4.7	3	7	3	2.0	1.0
3	2	-1	4.0	-3.1	3	4	-9	0.8*	-0.3	3	5	5	4.1	-2.7	3	7	4	1.7	-1.7
3	2	0	10.1	-11.3	3	4	-8	0.9*	0.7	3	5	6	4.3	-3.5	3	7	5	3.1	-2.5
3	2	1	3.2	-1.7	3	4	-7	0.9*	-0.4	3	5	7	3.7	-2.8	3	7	6	0.7*	-0.3
3	2	2	6.2	4.7	3	4	-6	4.8	4.3	3	5	8	3.2	3.3	3	7	7	1.4	0.8
3	2	3	2.4	1.6	3	4	-5	1.0*	1.1	3	5	9	1.5	1.0	3	8	-6	1.1	1.5
3	2	4	1.5	0.9	3	4	-4	1.9	-1.3	3	6	-9	0.4*	0.3	3	8	-5	1.9	1.0
3	2	5	8.6	8.0	3	4	-3	3.1	3.5	3	6	-8	0.7*	0.1	3	8	-4	0.7*	1.4
3	2	6	3.4	-2.7	3	4	-2	2.6	-3.0	3	6	-7	2.6	3.0	3	8	-3	5.2	-5.3
3	2	7	2.8	-1.6	3	4	-1	7.1	7.5	3	6	-6	0.9*	-1.4	3	8	-2	0.8	0.9
3	2	8	0.9*	-0.3	3	4	0	1.8	0.8	3	6	-5	0.9*	-0.4	3	8	-1	1.7	-0.8
3	2	9	0.8*	-0.5	3	4	1	2.2	-1.3	3	6	-4	3.8	-3.1	3	8	0	4.5	-5.0
3	2	10	5.5	5.7	3	4	2	0.9*	1.5	3	6	-3	5.6	-6.3	3	8	1	4.5	6.1
3	3	-10	3.0	-3.7	3	4	3	0.9	-1.9	3	6	-2	1.0*	0.1	3	8	2	1.1	-1.9
3	3	-9	0.8*	0.4	3	4	4	1.9	-0.7	3	6	-1	3.3	-3.5	3	8	3	1.3	-0.9
3	3	-8	6.3	6.5	3	4	5	7.3	-7.0	3	6	0	7.0	6.0	3	8	4	1.2	-0.5
3	3	-7	2.2	2.8	3	4	6	1.0	0.4	3	6	1	7.5	6.8	3	8	5	3.2	-4.2
3	3	-6	1.0*	-0.1	3	4	7	1.9	-1.2	3	6	2	1.0	0.4	3	9	-3	1.0	1.2
3	3	-5	11.1	13.0	3	4	8	0.8*	-0.4	3	6	3	1.7	0.9	3	9	-2	2.5	-2.0
3	3	-4	7.3	-6.6	3	4	9	0.7*	-0.1	3	6	4	2.5	1.8	3	9	-1	0.6	-0.3
3	3	-3	7.3	-6.6	3	4	10	0.5*	-0.2	3	6	5	2.4	-1.9	3	9	0	2.3	-2.6
3	3	-2	3.5	2.6	3	5	-9	5.6	-7.4	3	6	6	1.5	-1.0	3	9	1	3.9	-4.3
3	3	-1	5.1	-6.1	3	5	-8	2.6	2.8	3	6	7	0.7*	0.8	3	9	2	0.6*	0.6
3	3	0	9.4	-10.3	3	5	-7	4.7	3.2	3	6	8	1.6	-1.3	3	9	3	0.5*	1.5

were adjusted as variables in the least-squares refinements. The photographs and intensity standard were taken with the new Kodak 'No-Screen' film which was distributed in 1958. This film had an abnormally high background and its properties may have contributed to the possible errors in our intensity scale which are discussed below.

Unit cell and space group

The monoclinic unit cell dimensions at -95°C . are listed in Table 1. These values are in reasonable agreement with those found for the lower temperature at Houston. The calculated density, assuming four molecules per unit cell, is 1.222 g.cm.^{-3} . The reported density at -35° is 1.1894 g.cm.^{-3} (Rozenal, 1936). The absent reflections, ($h0l$, l odd and $0k0$, k odd) are characteristic of space group $P2_1/c$. The agreement finally achieved with the intensity data confirms this space group with each atom in general positions:

$$4(e): \pm(x, y, z; x, \frac{1}{2}-y, \frac{1}{2}+z).$$

Determination of the structure

The approximate structure was derived from the three-dimensional Patterson function. The first interpretation yielded four atoms whose 12 coordinates correspond reasonably well with the final result except that each y coordinate is associated with the wrong x and z . With this structure and certain variations of it the conventional unreliability index R could not be reduced below 0.50. A second interpretation based on the Harker section at $y=\frac{1}{2}$ and with y

coordinates calculated on the assumption of a dimer with reasonable bond distances yielded a trial structure with coordinates which differ by 0.03 or less from our final result.

The atomic scattering factors for the *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (1935) for hydrogen and of Hoerni & Ibers (1954) for carbon and oxygen were used in all structure factor calculations. In the least-squares refinement, the reflections were weighted as described by Hardgrove & Templeton (1959). The refinement was carried out with the IBM 650 computer using the nearly-diagonal program LS-II (Senko, 1957). The last few cycles were run by using a modification of the program similar to that described by Hardgrove (1959) which used the complete matrix.

First only C and O atoms were considered. After two cycles with the $0kl$ data and four cycles with all the data, R was 0.169. Three additional cycles gave little improvement, reducing R to 0.164. Hydrogen atoms were inserted assuming a C-H bond length of 1.08 Å, tetrahedral angles at carbon, and a staggered configuration for the hydrogen atoms of the methyl group relative to the substituents of the α -carbon atom. The addition of the hydrogen atom coordinates to the structure factor calculation decreased R to 0.151. However, certain large discrepancies between observed and calculated structure factors were noted. Five very strong reflections (011 , 021 , 024 , $11\bar{1}$, $11\bar{2}$) which were calculated as stronger than observed were removed from the calculation. After two more cycles, R was 0.116. These five reflections had biased the scale factor, and their removal allowed a more normal

distribution of positive and negative values of $|F_o| - |F_c|$.

Several additional cycles were run with the full matrix. These cycles resulted in no change of a coordinate by more than 0.0004, no improvement in R , and only a very minute decrease in the sum of the squared residuals.

The observed and calculated structure factors are compared with the corresponding values obtained at Houston in Table 2. There is a systematic discrepancy between the two sets of experimental data. In the work at Berkeley, the weak reflections tend to be estimated stronger and the strong reflections weaker than in the work of Scheuerman & Sass. Thus at least one of the intensity scales is defective. An examination of the calculated structure factors suggests that the fault is largely in the Berkeley data.

Table 3. *Hydrogen coordinates and temperature factors assumed for final calculation at Berkeley*

	x	y	z	B
H ₆	0.895	0.379	0.488	3.6 Å ²
H ₇	0.078	0.256	0.790	3.6
H ₈	0.445	0.247	0.729	3.6
H ₉	0.499	0.356	0.937	3.6
H ₁₀	0.579	0.481	0.828	3.6
H ₁₁	0.253	0.486	0.880	3.6

The coordinates for hydrogen which finally were used in the calculations are given in Table 3. They were estimated from assumed distances and angles as described before. The final atomic parameters are listed in Table 4. The standard deviations which are listed are those estimated by the method of least squares assuming that the discrepancies are random, and they include no allowance for the systematic nature of the errors.

Determination of the structure at Houston

Experimental

Crystals of propionic acid were grown in a sealed 0.3 mm. diameter Lindemann glass capillary mounted on a standard Weissenberg goniometer. The sample was frozen by a continuous stream of cold nitrogen gas obtained by boiling liquid nitrogen. The temperature of the gas stream could be regulated to within 1 °C. of any desired temperature between room temperature and about -140 °C. A single crystal was grown by first freezing the sample and then adjusting the nitrogen temperature to just below the melting point of propionic acid (-20.7 °C.). The frozen polycrystalline sample was then moved through a small zone heater until only a single seed crystal remained in the tip of the capillary. The tip of the capillary was then moved out of the region of the zone heater and the single crystal grew down the length of the capillary. The growth axis was always observed to be the a crystallographic axis. When a single crystal was obtained the temperature was reduced to

-135 ± 2 °C. All data were recorded at this temperature with Cu $K\alpha$ radiation on Kodak no screen medical X-ray film. It was determined from oscillation and Weissenberg photographs that the crystals were monoclinic and the extinctions, $h0l$ with l odd and $0k0$ with k odd indicate the space group $C_{2h}^2-P2_1/c$. The cell constants were obtained from sodium chloride calibrated rotation and zero layer Weissenberg photographs. a_0 for sodium chloride was taken to be 5.637 Å. The monoclinic angle β was determined by the method of angular lag (Buerger, 1942). The cell constants (Table 1) are in essential agreement with those reported at -95 °C. by Strieter & Templeton. The calculated density of 1.218 g.cm.⁻³ with four molecules per unit cell agrees favorably with the experimental density at -35 °C. of 1.189 g.cm.⁻³ (Rozenal, 1936). Subsequent refinement supported this space group with atom in the four fold general positions $4e$.

Treatment of data

Weissenberg photographs of the $h=0, 1$ and 2 layers were taken with sets of four films and the intensities of the various reflections were estimated visually employing a standard intensity strip. The camera had been modified to allow all of the various sets of data to be taken without disturbing the crystal. Because of this modification it was necessary to use two sets of film to record all of the data from each layer. Correlation of the intensities of the various sets of films was made by comparison to a photograph which contained 15 min. exposures of a 25 degree portion of each layer. The intensities were then corrected by the appropriate Lorentz, polarization and Tunell factors; absorption was neglected.

Because of the relatively short a axis (4.07 Å) and the planar character of the carboxyl group, it was anticipated that a [100] projection would present a reasonably resolved image of the molecule. The Patterson projection $P(vw)$ was calculated and subsequently yielded the solution of the trial structure. The major factor leading to the solution of the Patterson diagram was the assignment of near origin peaks to the vectors of the trigonal array of atoms in the carboxyl group. Once the orientation of this major portion of the molecule was established the other features of the Patterson could be explained by a structure consisting of hydrogen bonded dimers lying across a center of symmetry. The electron density projection $\rho(yz)$ calculated employing the observed structure factor magnitudes and signs based on proposed trial structure was well resolved and showed no questionable features.

The two dimensional parameters obtained from the electron density projection were then used as input parameters for a two-dimensional least-squares refinement. A total of 87 observed and 20 unobserved (too weak) reflections were used. The unobserved reflections were given a value of one-half the minimum observable value. These calculations were carried out

Table 4. *Final atomic parameters for propionic acid*

For each atom, the first line gives the results of Stricter & Templeton, the second line those of Scheuerman & Sass after conversion to the same orientation and origin

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	B
O ₁	0.9779	0.3196	0.5679	0.0009	0.0004	0.0003	3.0 Å ²
	0.9770	0.3186	0.5674	0.0027	0.0010	0.0008	3.4
O ₂	0.2222	0.5291	0.6258	0.0009	0.0004	0.0003	2.8
	0.2236	0.5291	0.6255	0.0027	0.0010	0.0008	3.2
C ₃	0.1554	0.3988	0.6450	0.0012	0.0005	0.0004	2.3
	0.1565	0.3997	0.6454	0.0018	0.0006	0.0005	3.0
C ₄	0.2717	0.3162	0.7560	0.0013	0.0005	0.0004	2.7
	0.2732	0.3143	0.7554	0.0017	0.0006	0.0005	3.4
C ₅	0.4127	0.4138	0.8571	0.0014	0.0006	0.0005	3.2
	0.4118	0.4177	0.8566	0.0026	0.0009	0.0007	3.5

on an IBM 704 computer using the Vand-Sly program. This program is a diagonal approximation including only the intra-atomic off diagonal elements of the normal equation matrix. A rather regrettable feature of the refinement was that only unit weights could be assigned to the observational equations. Individual isotropic temperatures are refined for all atoms. The carbon and oxygen form factors were those of McWeeny (1951). During the least squares refinement the 'reliability index' decreased from $R=0.370$ to $R=0.113$ and $\Sigma|F_o - F_c|^2$ decreased from 1,511 to 190.

The trial x parameters were determined in the following manner. The fact that the strongest observed reflections were the $11\bar{1}$ and $11\bar{2}$ suggested that the molecules probably were oriented nearly parallel to one of these planes, thus establishing the general tilt of the molecules. Using the projected bond distances determined from the refined y and z parameters and anticipated bond lengths, trial x parameters were readily calculated.

A total of 479 reflections (374 observed, 105 too weak to observe) were then used to refine all trial parameters in a complete three dimensional least squares treatment using the IBM 704 program described above. In the final stages of refinement, three reflections suffering from extinction (011 , 021 , $01\bar{1}$) were omitted from the calculation. During the course of the refinement the 'reliability index' decreased from $R=0.348$ to $R=0.148$ and the sum of the squares of the residuals decreased from 4,772 to 756. In the final two cycles of the refinement no positional parameter changed by more than 0.00003 units. The final calculated and observed structure factors are listed in Table 2. A summary of the final atomic parameters is presented in Table 4. The final calculated and observed structure factors are listed in Table 2.

Discussion of the structure

The molecules occur as dimers about centers of symmetry (Figs. 1 and 2) with no chemical bonding from one dimer to another. With the exception of the terminal carbon atom (C₅) the heavy atoms of the

entire dimer are coplanar within ± 0.01 Å. The perpendicular distance between successive planes is 3.36 Å. The C₄-C₅ bond makes an angle of 10.6° (Berkeley) or 12.5° (Houston) with its projection on the molecular plane. The corresponding distances of C₅ from this plane are 0.28 Å and 0.33 Å.

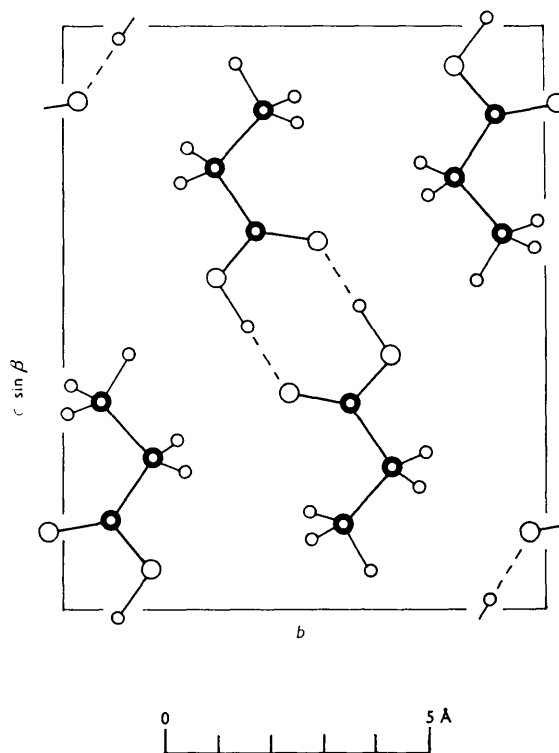


Fig. 1. Projection of the structure along $[100]$. The smallest circles represent hydrogen atoms at the positions assumed in the Berkeley calculations.

The bond distances and bond angles (Tables 5 and 6 and Fig. 3) are believed to be accurate within about 0.01 Å and 1° , respectively, in each determination. Except for the C₄-C₅ bond distance, there is no significant disagreement between the two sets of results. For this terminal C-C bond, one result (1.52 Å) is shorter than expected, and the other (1.55 Å) is

longer. The average result, 1.536 Å, is a normal C-C single-bond distance and is likely to be close to the correct value. That the C₃-C₄ bond (1.50 Å) is shorter is reasonable because of the proximity to the unsaturation of the C-O bonds. The hydrogen-bond length 2.64 Å and the C-O distances 1.23 Å and 1.32 Å are in accord with the structures of several other carboxylic acids (*Tables of Interatomic Distances*, 1958).

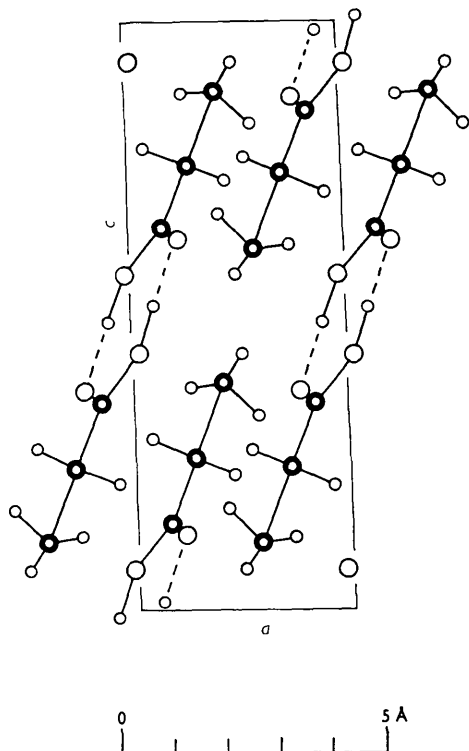


Fig. 2. Projection of the structure along [010].

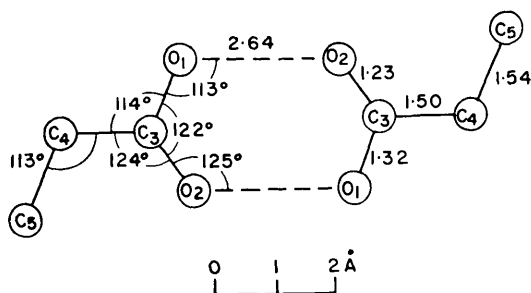


Fig. 3. Average bond distances in Å and bond angles. All the carbon and oxygen atoms are coplanar within experimental error except atoms C₅, which are about 0.30 Å from the plane of the others.

Table 5. Bond distances

Atoms	Distance		Average
	S. & T.	S. & S.	
C ₃ -O ₁	1.313 Å	1.336 Å	1.324 Å
C ₃ -O ₂	1.230	1.222	1.226
C ₃ -C ₄	1.499	1.504	1.502
C ₄ -C ₅	1.522	1.551	1.536
O ₁ -H...O ₂	2.645	2.643	2.644

Table 6. Bond angles

Atoms	Angle		Average
	S. & T.	S. & S.	
O ₂ -O ₁ -C ₃	112.9°	112.7°	112.8°
O ₁ -O ₂ -C ₃	124.9	125.1	125.0
O ₁ -C ₃ -O ₂	122.2	122.2	122.2
O ₁ -C ₃ -C ₄	114.2	113.2	113.7
O ₂ -C ₃ -C ₄	123.6	124.5	124.0
C ₃ -C ₄ -C ₅	114.2	111.8	113.0

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