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CRYSTAL STRUCTURE OF PROPIONIC ACID

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May 23, 1961

Crystal Structure of Propionic Acid^{*}By Frederick J. Strieter⁺ and David H. TempletonLawrence Radiation Laboratory and Department of Chemistry,
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According to single-crystal three-dimensional X-ray data, propionic acid crystals at -95°C are monoclinic, space group $P2_1/c$, with $a = 4.04 \pm 0.04$, $b = 9.06 \pm 0.01$, $c = 11.00 \pm 0.01 \text{ \AA}$, $\beta = 91^{\circ} 15' \pm 8'$. Atomic coordinates were refined by least-squares methods. Propionic acid molecules occur in the crystal as centric and nearly planar dimers with hydrogen bonds of length $2.64 \text{ \AA}$. Other bond lengths are: $\text{C}-\text{O}$, 1.23 and $1.31 \text{ \AA}$; $\text{C}-\text{C} (\alpha)$, $1.50 \text{ \AA}$; $\text{C}-\text{C} (\beta)$, $1.52 \text{ \AA}$, all with standard deviations of about $0.01 \text{ \AA}$.

^{*}Work done under the auspices of the U. S. Atomic Energy Commission.

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Introduction

The crystal structures of the normal fatty acids of low molecular weight have been rather neglected until recently. Formic acid (Holtzberg, Post and Fankuchen, 1953) and acetic acid (Jones and 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 and 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 to examine the structures of propionic and butyric acid crystals (Strieter, 1959). These crystals have different structures, but both contain dimers. Independently, Scheuerman and Sass (196x) determined the structure of propionic acid with results in general agreement with ours as described in the companion paper. They made a preliminary study of butyric acid before learning of our results and have also found that valeric acid has a structure which closely resembles that of propionic acid (Sass, 1961).

Experimental Procedure

Propionic acid ($\text{CH}_3\text{CH}_2\text{COOH}$) was studied with a modified Weissenberg camera (Olovsson and 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 CuK radiation, in some cases filtered with Ni. Unit cell dimensions were obtained from the uncalibrated rotation photograph and from a zero-layer Weissenberg photograph calibrated (Pabst, 1957) with quartz ($a = 4.913 \text{ \AA}$). The monoclinic angle, β , was determined by the method of angular lag (Buerger, 1942). Because the crystals always grew with the a axis parallel to the capillary axis, we have photographs only for this orientation, and the a axis is less accurately determined than are the other axes.

About 600 independent intensities were estimated visually by comparison with a set of timed exposures of one reflection of the same crystal. About 140 other reflections were listed as too weak to be observed. These observations were based on Weissenberg films for layers with h ranging from 0 to 3. Because of the symmetry and the fact that our camera recorded only one side of the Weissenberg pattern, two sets of films were used to record each upper layer to include all the reflections. The scale factors for the various layers 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:

$$\begin{aligned} a &= 4.04 \pm 0.04 \text{ \AA} & b &= 9.06 \pm 0.01 \text{ \AA} & c &= 11.00 \pm 0.01 \text{ \AA} \\ \beta &= 91^{\circ} 15' \pm 8' \end{aligned}$$

These values are in reasonable agreement with those reported for a lower temperature by Scheuerman and Sass (196x). The calculated density, assuming

four molecules per unit cell, is 1.234 g cm^{-3} . The reported density at -35° is 1.1894 g cm^{-3} (Rozenal, 1936). The absent reflections 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:

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

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 $y = 1/2$ 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 of the Internationale Tabellen (1935) for hydrogen and of Hoerni and 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 and 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 Okl 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 structure factors are listed in Table 1. A sample of the observed and calculated structure factors, arranged in order of increasing diffraction angle, are compared with the corresponding values obtained by Scheuerman and Sass in Table 2. There is a systematic discrepancy between the two sets of experimental data. In our work, the weak reflections tend to be estimated stronger and the strong reflections weaker than in the work of Scheuerman and 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 our data.

The final atomic parameters are listed in Table 3. The coordinates listed for hydrogen are those that were used in the calculations. They were estimated from assumed distances and angles as described before. 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.

Table 1. Observed structure factors, each multiplied by 10.

An asterisk (*) indicates the observational limit for an unobserved reflection. A structure factor followed by the letter "X" was omitted from the final refinement cycles. The 304 reflections so marked were inadvertently omitted from all of the calculations. By error, reflection 2.5.11 was treated as unobserved in all of the calculations.

H = 0											
K=0	1	2	3	4	5	6	7	8	9	10	11
L=0	97			32		90		86		62	
1	168X	255X	98	137	165	48	22	94	16*	89	21
2	128	92	14	167	29	196	49	60	16*	78	14
3		76	123	134	79	13*	72	45	67	41	42
4	285	179	287X	51	12	48	69	98	40	40	13
5		145	50	12*	198	10*	147	16*	118	14	11*
6	92	74	177	48	32	74	127	104	76	27	
7		54	14*	102	83	36	16*	36	20	41	
8	129	15*	126	16*	36	23	32	21	13*	10*	
9		22	62	101	37	16	48	14*	79		
10	136	75	16*	16*	47	15*	14*	78	30		
11		35	94	34	29	13*	40				
12	14*	25	63	13*	32	18					
13		12*	23	34	8*						

H = 1											
K=0	1	2	3	4	5	6	7	8	9	10	11
L=-13	11*		57	6*							
-12	13*	67	22	27	11*	9*					
-11		37	36	50	27	38	31				
-10	42	22	59	66	34	14*	13*	47			
-9		89	16*	28	45	15*	14*	13*	10*		
-8	25	49	65	69	16*	78	34	14	47	49	
-7		51	14*	77	43	176	64	21	41	62	
-6	248	37	57	144	38	48	65	124	36	12*	9*
-5		246	79	58	96	48	15*	16	22	23	61
-4	82	84	10*	44	13*	109	34	80	16*	57	11*
-3		8*	127	165	196	53	60	41	50	15*	53
-2	375	409X	131	109	73	108	76	38	23	99	22
-1		496X	80	202	58	85	75	46	62	15*	13
0			140	6*	22	102	99	98	34	103	15
1	110	62	153	151	8*	93	10*	62	26	17	6*
2	29	67	245X	122	100	16	39	36	73	30	8*
3		237X	112	234	108	145	114	25	71	54	17
4	27	209	43	167	40	36	29	206	10*	29	7*
5		110	111	153	99	100	96	10*	52	41	6*
6	62	8*	115	20	48	22	10*	10*	46	11	
7		135	42	98	70	35	35	22	26	14	
8	106	77	65	39	29	31	38	61	39	61	
9		115	72	55	10*	29	51	25	26		
10	51	93	33	10*	27	22	27	31			
11		42	16	48	41	8*	21	3*			
12		29	8*	23	10	21					
13		54	6*								

H = 2										
K=0	1	2	3	4	5	6	7	8	9	10
L=-12	25		12	18	32					
-11		41	42	16	36					
-10	61	19	14	29	17	24	7*			
-9		10	22	10*	86	46	8*	6*		
-8	79	41	28	20	58	32	96	25	42	
-7		108	69	14	95	30	31	9*	34	
-6	136	19	51	21	37	33	35	33	8*	46
-5		8*	8*	100	32	14	59	10*	50	7*
-4	57	132	135	11	114	71	10*	10*	51	52
-3		178	294	53	65	9	43	10	10	14
-2	361	87	15	17	93	13	10*	101	51	44
-1		58	43	110	27	41	80	10*	78	9*
0		64	143	19	61	18	27	70	25	9*
1		107	56	187	128	74	10*	21	29	47
2	9	74	194	50	27	34	157	119	65	22
3		128	59	8*	148	10*	132	11*	90	9*
4	126	94	152	24	21	20	21	55	39	16
5		99	9*	52	73	15	30	29	9*	7*
6	111	96	65	28	18	81	44	20	8*	52
7		109	96	49	37	42	28	16	54	4*
8	216	43	15	28	10	23	35	20	37	
9		45	48	10*	52	32	8*	19		
10	39	10	29	19	9*	35	6*			
11		23	42	31	74	25				
12	58	27	53	36	4*					

H = 3									
K=0	1	2	3	4	5	6	7	8	9
L=-11	22	6*							
-10	8*	31	8	30	32				
-9		9*	42	8*	56	4*			
-8	65	28	17	63	9*	26	7*		
-7		28	14	22	9*	47	26	11	
-6	25	33	64	10*	48	9*	9*	42	11
-5		22	69	111	10*	10*	9*	23	19
-4	81	132	56	73	19	10*	38	43	7*
-3		67	11	73	31	41	56	34	52
-2	92	6*	75	35	26	26	10*	46	8
-1		77	40	51	71	41	33	19	17
0		25	101	94	18	89	70	40	45
1		12	32	72	22	142	75	27	45
2	150X	35	62	70	9*	10*	10	85	11
3		103	24	48	9	10*	17	20	13
4	90X	8*	15	60	19	50	25	17	12
5		45	86	56	73	41	24	35	32
6	142X	90	34	28	10	43	15	7*	
7		101	28	34	19	37	7*	14	
8	34X	19	9*	20	8*	32	16		
9		15	8*	21	74	15			
10	20X	20	55	24	5*				
11		36							

Table 2. Sample of observed and calculated structure factors

<u>hkl</u>	This work		Scheuerman and Sass	
	$\underline{F_o}$	$\underline{F_c}$	$\underline{F_o}$	$\underline{F_c}$
021	25.5	-43.7	33.9	41.3
112	6.7	-5.6	5.8	7.4
12 $\bar{3}$	12.7	10.2	10.3	-11.6
1 $\bar{1}$ 4	4.0	-3.0	3.2	-2.5
24 $\bar{2}$	9.3	-8.2	7.9	-5.8
21 $\bar{7}$	10.8	-12.1	10.4	-12.0
15 $\bar{6}$	4.8	-4.9	4.5	4.8
039	10.1	9.6	8.7	9.1
174	20.6	-21.5	20.1	19.5
208	21.6	-22.0	25.4	-20.0
0.0.10	13.6	-14.0	12.4	-12.8
18 $\bar{3}$	5.0	-4.7	4.0	3.6
068	3.2	-2.3	2.6	-2.4
229	4.8	4.7	5.4	-3.9
28 $\bar{2}$	5.1	-4.4	3.9	-4.2
0.3.11	3.4	-3.0	2.7	-2.2
095	1.4	1.2	1.9	1.1
2.5.10	3.5	-3.2	4.0	3.1
0.3.13	3.4	-2.8	2.3	-2.6
1.3. $\bar{13}$	5.7	-5.5	4.4	4.5

Table 3. Final atomic parameters for propionic acid

The values in parentheses are those of Scheuerman and Sass, converted to our method of designation

	x	y	z	σ_x	σ_y	σ_z	B, A^2
O_1	0.9779	0.3196	0.5679	0.0009	0.0004	0.0003	3.0
	(0.9770)	(0.3186)	(0.5674)				(3.4)
O_2	0.2222	0.5291	0.6258	0.0009	0.0004	0.0003	2.8
	(0.2236)	(0.5291)	(0.6255)				(3.2)
C_3	0.1554	0.3988	0.6450	0.0012	0.0005	0.0004	2.3
	(0.1565)	(0.3997)	(0.6454)				(3.0)
C_4	0.2717	0.3162	0.7560	0.0013	0.0005	0.0004	2.7
	(0.2732)	(0.3143)	(0.7554)				(3.4)
C_5	0.4127	0.4138	0.8571	0.0014	0.0006	0.0005	3.2
	(0.4118)	(0.4177)	(0.8566)				(3.5)
H_6	0.895	0.379	0.488	assumed			3.6
H_7	0.078	0.256	0.790	assumed			3.6
H_8	0.445	0.247	0.729	assumed			3.6
H_9	0.499	0.356	0.937	assumed			3.6
H_{10}	0.579	0.481	0.828	assumed			3.6
H_{11}	0.253	0.486	0.880	assumed			3.6

The atomic parameters found by Scheuerman and Sass are listed in parentheses in Table 3, after conversion to our choice of origin. Because of the discrepancy in intensity scales, the temperature parameters are substantially different in the direction opposite to that expected from the respective temperatures of measurement. Atoms O_1 , O_2 , and C_3 are found in the same place within 0.01 Å in the two experiments. The locations of C_4 and C_5 disagree by 0.02 Å and 0.04 Å, respectively, because of discrepancies in the y coordinates. Part of this difference may be an effect of the temperature, but it is unlikely that it all can be explained in this way.

Discussion of the Structure

The molecules occur as dimers about centers of symmetry (Fig. 1) with no chemical bonding from one dimer to another. The bond distances and bond angles (Fig. 2) are believed to be accurate within about 0.01 Å and 1°, respectively. Except for the C_4 - C_5 bond distance, there is no significant disagreement with the results of Scheuerman and Sass (196x). Our result for this terminal C-C bond, 1.52 Å, is hardly shorter than the distance 1.53 Å found in saturated hydrocarbons (Bartell, 1959). The value 1.55 Å found by Scheuerman and Sass seems to be too long. That the C_3 - C_4 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 1.31 Å are in accord with the structures of several other carboxylic acids (Tables of interatomic distances, 1958).

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

MU-23586

Fig. 2. Bond distances in Å and bond angles.

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