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THE CRYSTAL STRUCTURES OF SEVERAL
ORGANIC COMPOUNDS

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Frederick J. Strieter

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September 18, 1959

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ABSTRACT

Carbon Tetrabromide-p-Xylene

The structure of the 1-1 addition compound of carbon tetrabromide and para-xylene ($\text{CBr}_4 \cdot \text{CH}_3\text{-C}_6\text{H}_4\text{-CH}_3$) has been determined by three-dimensional single-crystal x-ray diffraction techniques. The compound crystallizes in an orthorhombic unit cell with the following dimensions: $a = 8.476 \pm 0.03$, $b = 8.894 \pm 0.03$, $c = 17.465 \pm 0.05 \text{ \AA}$. There is very little distortion of the constituent molecules, and the main intermolecular binding force in the crystal seems to be the interaction of the π electron system of the aromatic nucleus with half of the bromine atoms of the carbon tetrabromide. Each aromatic ring has two bromine atoms, one on each side, at a distance of $3.34 \pm 0.02 \text{ \AA}$ from the center of the ring. The average distance from the bromine atom to the carbon atoms of the aromatic nucleus is $3.62 \pm 0.02 \text{ \AA}$.

Propionic Acid

According to single crystal three-dimensional x-ray data, propionic acid crystals at -95°C have monoclinic symmetry, space group $\text{P}2_1/\text{c}$ ($\text{C}_{2\text{h}}^5$), with $a = 4.042 \pm 0.040$, $b = 9.063 \pm 0.010$, $c = 10.998 \pm 0.010 \text{ \AA}$ and $\beta = 91^\circ 15' \pm 8'$. Least-squares methods were used to refine an approximate structure derived from a Patterson synthesis. The results show that propionic acid forms nearly planar dimers in the solid, with an $\text{O-H}\cdots\text{O}$ bond of 2.645 \AA , a C=O bond of 1.230 \AA , a C-O bond of 1.313 \AA and C-C bonds of 1.499 \AA and 1.522 \AA , all with standard deviations of less than $\pm 0.010 \text{ \AA}$.

n-Butyric Acid

According to a single crystal x-ray analysis of three-dimensional data at -43°C , n-butyric acid crystallizes in a monoclinic space group, $C2/m$, with the following unit cell dimensions: $a = 8.014 \pm 0.080 \text{ \AA}$, $b = 6.815 \pm 0.020 \text{ \AA}$, $c = 10.145 \pm 0.030 \text{ \AA}$, and $\beta = 111^{\circ}27' \pm 15'$. Least-squares methods were used to refine an approximate structure derived from a Patterson synthesis. Within experimental error, two molecules are hydrogen bonded together to form a planar dimer which is perpendicular to the b axis. The structure gives a hydrogen bond 2.63 \AA long, a C=O bond of 1.19 \AA , a C-O bond of 1.34 \AA , and C-O bonds of 1.48 \AA , 1.52 \AA and 1.49 \AA , all with standard deviations of less than $\pm 0.02 \text{ \AA}$.

THE CRYSTAL STRUCTURE OF CARBON TETRABROMIDE · p-XYLENE

Introduction

Several compounds of halogenated methanes with benzene and various methyl benzenes have been reported in the literature (Kapustinskii, 1947; Egan and Luthy, 1955). Little was known about the crystal structure or the nature of the bonding in these compounds, although various theories had been proposed to account for the bonding in molecular addition compounds (Andrews, 1954, p. 761). It was felt that an investigation of the crystal structure would help in the understanding of the binding forces.

An interesting phenomenon in this series of compounds is the relative stability at room conditions. For example, the addition compounds formed with carbon tetrabromide by both the meta and ortho isomers of xylene are liquids at room temperature. The compound with the para isomer, however, is a solid. Thus, in an attempt to gain further information about the nature of the bonding forces in this type of compound and to learn more about the selectivity of solid compound formation in the series, this structure determination was undertaken.

Experimental Procedures

The carbon tetrabromide · p-xylene compound ($\text{CBr}_4 \cdot \text{H}_3\text{C} \text{---} \text{C}_6\text{H}_4 \text{---} \text{CH}_3$) was selected for this investigation since it is a solid at room temperature (m. p. 53°C). The compound was prepared by mixing approximately equimolar amounts of 99.85% pure p-xylene and Eastman carbon tetrabromide. A slight excess of p-xylene was added, and the mixture was warmed slightly to promote the solubility of the carbon tetrabromide. On cooling, the desired compound grew as thin, flat, square platelets. The compound has a high vapor pressure, and sublimates readily if exposed to the air. Therefore the crystals were preserved by being kept in contact with the mother liquor. Since platelets were unsuitable for good x-ray data in the Weissenberg camera, one of the platelets was cut into small rectangular needles. These needles were then sealed in small glass capillaries.

After several attempts, one of them was aligned about a $[110]$ axis. Rotation and zero-through fifth-layer Weissenberg photographs were recorded by multiple-film techniques. Upon analysis of the data it was decided that they were inaccurate because of absorption. The irregular shape of the crystal made it difficult to correct for this absorption effect.

To overcome this problem, one of the large platelet crystals was melted, and the liquid was sealed in a capillary, 0.3 mm in diameter. It crystallized immediately as a powder. The capillary was mounted on a Weissenberg goniometer and placed on the stage of a polarizing microscope. A stream of warm air was passed over the capillary to melt the material at one end. The temperature of the air stream was gradually reduced, and after several attempts a satisfactory single, cylindrical crystal was grown. The b axis of the crystal was within a few degrees of being parallel to the capillary axis. This crystal was mounted on the Weissenberg camera and lined up about the b axis by means of oscillation photographs. A rotation pattern, zero - through fifth-layer uncalibrated, multiple-film Weissenberg exposures, and a zero-layer, single-film quartz-calibrated Weissenberg photograph were taken using Cu K α radiation ($\lambda = 1.5418\text{\AA}$).

Unit Cell and Space Group

The first set of pictures (about the $[110]$ orthorhombic axis) at first glance appeared to show monoclinic symmetry, with unit cell dimensions of $a = 6.145$, $b = 17.465$, $c = 6.145\text{\AA}$ and $\beta = 92^{\circ}48'$. However, closer inspection of the pictures showed that the a and c axes of the primitive monoclinic cell were the face diagonals of a C-centered orthorhombic cell. The extinctions suggested that the most likely space groups were $Cmcm(D_{2h}^{17})$, $Cmc2_1(C_{2v}^{12})$, and $C2cm(C_{2v}^{16})$ (this space group is listed with a different orientation of axes as $Ama2$ in the International Tables). The higher symmetry group, $Cmcm$, seemed to be the most desirable choice since the symmetry of the constituent molecules was best satisfied in this space group. The subsequent refinements demonstrated that this was the correct choice.

The dimensions of the centered orthorhombic unit cell were determined from both sets of quartz calibrated zero-layer Weissenberg photographs, by using the method of angular lag (Buerger, 1942, p.377) to determine the angle between the $[110]$ and $[1\bar{1}0]$ axes. The dimensions are $a = 8.476 \pm .03$, $b = 8.894 \pm .03$, and $c = 17.465 \pm .05 \text{ \AA}$. By using these cell dimensions and the molecular volumes of liquid p-xylene and solid carbon tetrabromide, it was calculated that there were 3.6 molecules per unit cell. This indicated that there were four molecules per unit cell, since the volume of the solid compound would tend to be smaller than that of the separate constituents. The calculated density for four molecules per unit cell is 2.209 g cm^{-3} .

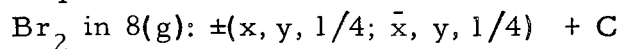
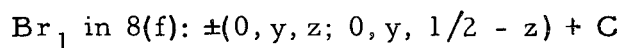
Determination of the Structure

There were 481 observed and 157 unobserved independent reflections in the portion of reciprocal space photographed about the $[110]$ axis. Intensities were estimated visually by comparison with a standard film. The corrections for Lorentz, polarization, and velocity effects were made with the INCOR routine for the IBM 650. Interlayer scale factors were determined from the corrected intensities of reflections that occurred on more than one layer. All structure factor calculations were made by using the atomic scattering factors of Thomas and Umeda (1957) for bromine, Hoerni and Ibers (1954) for carbon, and the Internationale Tabellen (1935) for hydrogen. The least squares refinements were made with the LS II program (Senko, 1957).

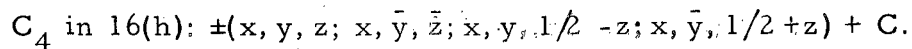
In space group Cmcm, the fourfold positions are at centers of symmetry or on intersections of two mirror planes. Since the carbon tetrabromide molecule is tetrahedral, its carbon atom cannot be at a center of symmetry. Therefore these carbon atoms, denoted as C_3 , are placed in position 4 (c) of the International Tables (1952):

$$C_3 \text{ in } \pm (0, y, 1/4) + C.$$

The bromine atoms can then only be placed on the mirror planes in the two sets of positions,



A three dimensional Patterson synthesis based on the observed reflections was calculated by using the IBM 701 Fourier program of Jones, Dodge, and Templeton (Dodge, 1958). This Patterson map showed large peaks corresponding to bromine atoms at 0, 0.20, 0.34, and 0.19, 0.45, 0.25, and a carbon atom at 0, 0.325, 0.25. The signs of the structure factors calculated with only the carbon tetrabromide molecule as a trial structure were attached to the observed structure factors, and a three dimensional Fourier synthesis was computed. From this, the p-xylene molecule was determined to be perpendicular to the yz plane with its center at the origin (2/m). For this arrangement, the other carbon atoms must be distributed in two more sets of 8(f) (atoms C₅ and C₆) and in one general set,



Several cycles of least squares refinement were run based on this structure, but the reliability index,

$$R_1 = \left(\sum \left| |F_o| - |F_c| \right| \right) \div \left(\sum |F_o| \right),$$

did not fall below 0.20. Since no correction had been made for absorption, it was decided to grow a cylindrical crystal and make the necessary absorption correction.

There was a total of 493 reflections in the portion of reciprocal space photographed about the $[010]$ axis. The 298 observed (195 unobserved) reflections from the cylindrical crystal were gathered and corrected in the same manner as before. In addition, the method outlined by Bond (1959) was used to correct for absorption. For this crystal, μr was 2.28; Bradley's table (Klug and Alexander, 1952, p. 155) was used for the absorption coefficients. By using the parameters previously determined, additional least squares refinements were carried out. After 15 cycles the parameters listed in Table I were obtained.

Table I

Final parameters obtained by using only carbon and bromine atoms							
	<u>x</u>	<u>y</u>	<u>z</u>	<u>B</u>	<u>σ_x</u>	<u>σ_y</u>	<u>σ_z</u>
Br ₁	0	.2040	.3393	7.23	-	.0005	.0002
Br ₂	.1841	.4497	1/4	7.36	.0006	.0005	-
C ₃	0	.332	1/4	6.35	-	.007	-
C ₄	.139	.931	.020	4.98	.002	.003	.001
C ₅	.0	.864	.048	4.63	-	.004	.002
C ₆	0	.733	.091	6.20	-	.005	.002

R₁ = .147 R₂ = .140 R₃ = .232 based on all 493 reflections

Bond distances

C ₃ - Br ₁	1.94 Å	C ₄ - C ₄	1.40 Å
C ₃ - Br ₂	1.87 Å	C ₄ - C ₅	1.42 Å
Br ₁ - Br ₁ '	3.11 Å		
Br ₁ - Br ₂	3.11 Å	C ₅ - C ₆	1.40 Å
Br ₂ - Br ₂ '	3.11 Å		

$$R_1 = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|}, \quad R_2 = \left[\frac{\sum (|F_o| - |F_c|)^2}{\sum (F_o)^2} \right]^{1/2}$$

$$R_3 = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w(F_o)^2} \right]^{1/2}$$

At this point, since the structure appeared to be correct but the agreement was not as good as desired, hydrogen positions were calculated, based on a C-H bond length of 1.08 Å and assuming normal placement of the hydrogen atoms in the aromatic ring and methyl group. The hydrogen atoms were placed in two sets of general positions,

H₇ and H₈ in 16(h),

and one set of special positions,

H₉ in 8(f).

The symmetry and bond geometry permit two choices of orientation of the methyl group. This orientation was determined from a difference Fourier synthesis ($|F_o| - |F_c|$ synthesis). Seven additional least-squares refinement cycles were run which included the hydrogen atoms but did not allow their parameters to change. The final parameters obtained are listed in Table II together with the standard deviations and bond distances. Table III shows the observed and calculated structure factors for the final structure.

Discussion

The bond distances and angles in the carbon tetrabromide molecule do not show large deviations from the expected values. The deviations from the expected bond angles and lengths in the *p*-xylene molecule are larger, but within the fairly large standard deviations. The accuracy of the bond lengths and angles is not great, but it is good enough so that the main features of the structure are apparent.

The most interesting feature of the structure is the packing arrangement of the carbon tetrabromide and *p*-xylene molecules. The molecules form a zigzag chain which has the lengthwise direction parallel to the *c* axis (see Fig. 1). The closest approach of the bromine atoms to the ring is shown in Fig. 2. Since the aromatic ring is planar within experimental error, Figs. 1 and 2 are drawn so that the ring is planar.

Table II

Final parameters for carbon tetrabromide • p-xylene							
	<u>x</u>	<u>y</u>	<u>z</u>	<u>B</u>	σ_x	σ_y	σ_z
Br ₁	0	.2034	.1608	7.59	-	.0005	.0002
Br ₂	.1840	.4506	1/4	7.60	.0005	.0005	-
C ₃	0	.331	1/4	5.28	-	.006	-
C ₄	.139	.932	.0193	5.66	.003	.003	.001
C ₅	0	.872	.0497	5.16	-	.004	.001
C ₆	0	.732	.0920	7.45	-	.005	.002
H ₇	.248	.880	.041	5.94	assumed		
H ₈	.106	.667	.077	5.94	assumed		
H ₉	0	.759	.147	5.94	assumed		

R₁ = .135 R₂ = .144 R₃ = .196 for all 493 reflections

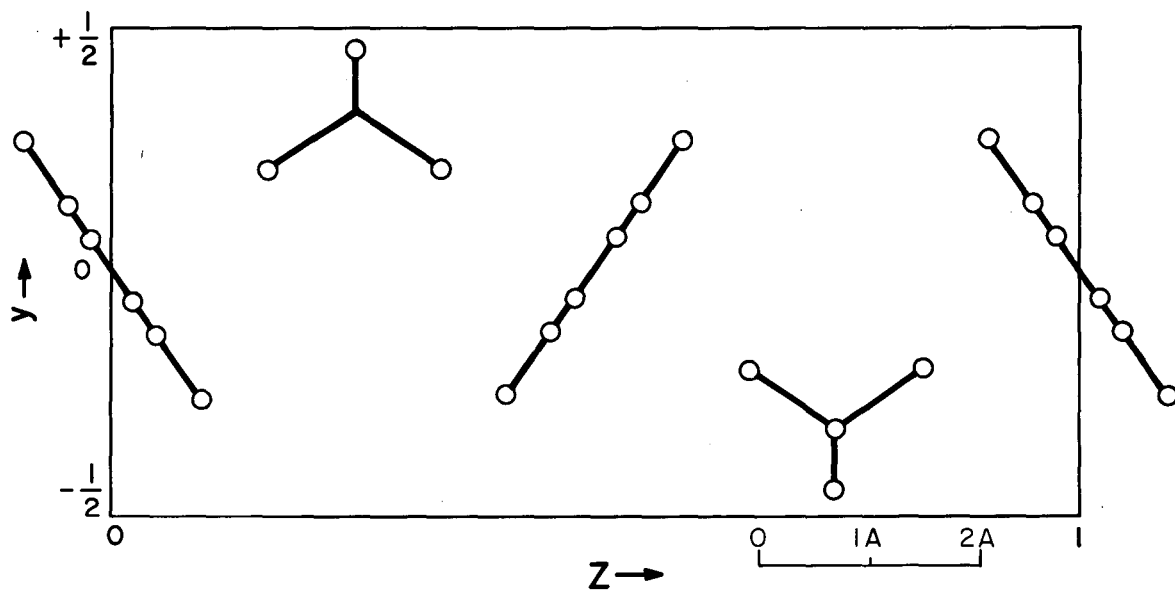
Bond distances

Br ₁ - Br ₁ '	3.116±.010 ^o Å		
Br ₂ - Br ₂ '	3.119±.010 ^o Å		
Br ₁ - Br ₂	3.114±.008 ^o Å	C ₄ - C ₄	1.39±.04 ^o Å
C ₃ - Br ₁	1.93±.03 ^o Å	C ₄ - C ₅	1.40±.03 ^o Å
C ₃ - Br ₂	1.89±.03 ^o Å	C ₅ - C ₆	1.45±.06 ^o Å

Table III. Observed and calculated structure factors for carbon tetrabromide · p-xylene.

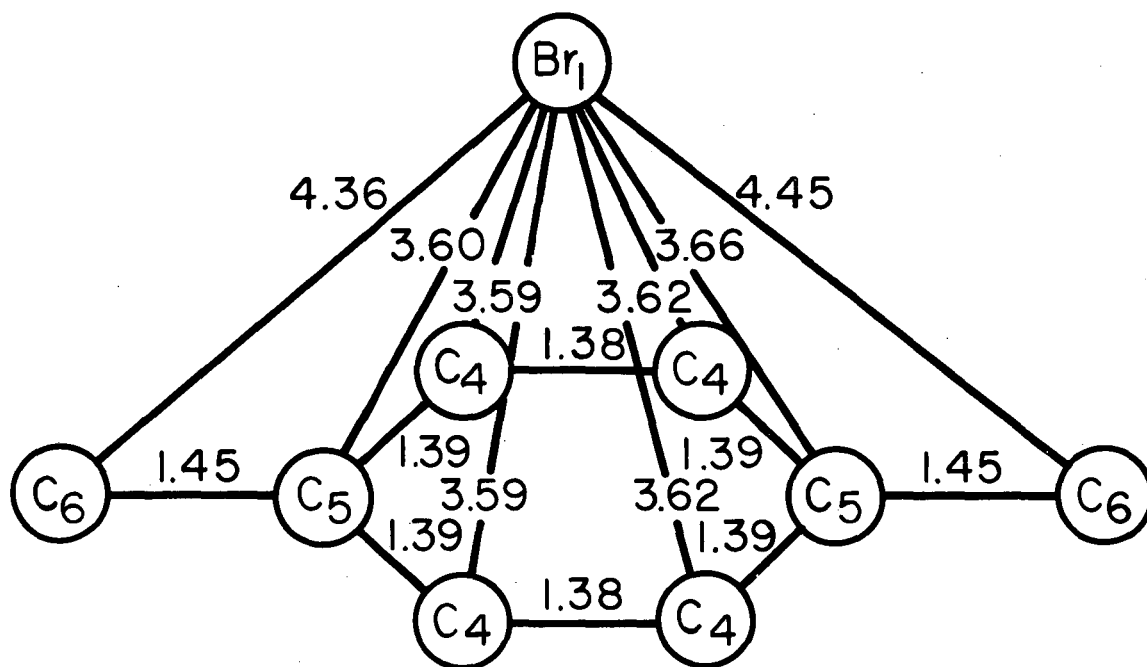
* indicates minimum observable structure factor.

h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	
0 0 0	8160		5 1 0	665	522-	4 2 16	136	130	5 3 6	178	164-	4 4 14	116	21	
0 0 4	1175	1535	5 1 1	955	968-	4 2 17	112*	25	5 3 7	533	609	4 4 15	110*	53	
0 0 8	167*	143-	5 1 2	689	667-	4 2 18	94*	34-	5 3 8	133*	83-	4 4 16	93*	69-	
0 0 12	1076	1166	5 1 3	381	325	4 2 19	85*	40-	5 3 9	165	177-	4 4 17	137	131-	
0 0 16	1622	1854-	5 1 4	934	879-	4 2 20	40*	16-	5 3 10	308	392	4 4 18	28*	16	
0 0 20	1112	1388	5 1 5	423	496	6 2 0	145*	143-	5 3 11	128*	19-	4 4 19	30*	16	
0 0 24	443	553-	5 1 6	738	731	6 2 1	145*	53	5 3 12	234	243-	6 4 0	319	227	
0 0 28	21	16	5 1 7	175	232-	6 2 2	212	112-	5 3 13	157	129-	6 4 1	561	601	
0 0 32	190*	74-	5 1 8	626	589-	6 2 3	236	244-	5 3 14	111	76	6 4 2	220	190-	
0 0 36	154*	137	5 1 10	276	209	6 2 4	718	647	5 3 15	122	94	6 4 3	239	192-	
2 0 0	1315	1461	5 1 11	392	438	6 2 5	503	584	5 3 16	90*	22	6 4 4	137*	53-	
2 0 2	569	557	5 1 12	147	215-	6 2 6	606	552-	5 3 17	80	129*	6 4 5	132*	39-	
2 0 4	2142	2558-	5 1 13	199	226-	6 2 7	288	281-	5 3 18	64*	23-	6 4 6	132*	32	
2 0 6	1862	2136	5 1 14	154*	174	6 2 8	303	300	5 3 19	37*	43	6 4 7	107*	16	
2 0 8	981	1155-	5 1 15	147*	45-	6 2 9	182	155	7 3 0	199	181-	6 4 8	17*	16	
2 0 10	330	191-	5 1 16	129*	139-	6 2 10	27*	16	7 3 1	247	240	6 4 9	107*	16	
2 0 12	289	174	5 1 17	119*	38	6 2 11	140*	17	7 3 2	90	34	6 4 10	159	60	
2 0 14	226*	226	7 1 0	350	336	6 2 12	133*	42-	7 3 3	2	89*	16-	6 4 11	85	54
2 0 16	389	398-	7 1 1	213	282-	6 2 13	121*	32	7 3 4	127	206	6 4 12	71	111	
2 0 18	185	238	7 1 2	18*	16	6 2 14	112*	76-	7 3 5	178	40-	6 4 13	108	232-	
2 0 20	5*	16-	7 1 3	168*	44	6 2 15	103*	100-	7 3 6	178	225-	6 4 14	12	111	
4 0 0	1252	1350	7 1 4	119	100	6 2 16	91	121	7 3 7	122*	147	6 4 15	137	162	
4 0 2	610	638-	7 1 5	381	374	6 2 17	73*	73	7 3 8	101	114	6 4 16	79*	16-	
4 0 4	886	1020-	7 1 6	168*	82	6 2 18	61*	68-	7 3 9	170	143	6 4 17	79*	16-	
4 0 6	687	687	7 1 7	252	162-	8 2 0	421	380-	7 3 10	106*	89	6 4 18	31*	16	
4 0 8	325	380-	7 1 8	161*	46	8 2 1	266	208-	7 3 11	98*	74-	6 4 19	31*	16	
4 0 10	529	540-	7 1 9	154*	54-	8 2 2	324	297	7 3 12	90*	32-	6 4 20	55*	20-	
4 0 12	411	326	7 1 10	154*	86-	8 2 3	182	136	7 3 13	82*	66	6 4 21	55*	20-	
4 0 14	217*	19-	7 1 11	175	177	8 2 4	94	24-	7 3 14	74*	17-	8 4 0	116*	20-	
4 0 16	190*	150-	7 1 12	129*	50	8 2 5	133*	62	9 3 0	98*	54-	8 4 1	138	29-	
4 0 18	108	120	7 1 13	119*	48-	8 2 6	127*	46	9 3 1	64	115	8 4 2	23*	16	
4 0 20	108*	58	7 1 14	108*	26-	8 2 7	121*	70	9 3 2	90*	24-	8 4 3	206	194	
6 0 0	1274	1436	7 1 15	98*	32-	8 2 8	103*	80-	9 3 3	90*	40-	8 4 4	110*	115-	
6 0 2	669	655-	9 1 0	140*	132-	8 2 9	112*	48-	9 3 4	117	89	8 4 5	231	214-	
6 0 4	253	183	9 1 1	140*	91-	8 2 10	182	168	9 3 5	11*	16-	8 4 6	102	89	
6 0 6	226*	45	9 1 2	140*	71-	8 2 11	151	115	9 3 6	141	109-	8 4 7	239	215	
6 0 8	276	239	9 1 3	47*	16	8 2 12	145	137-	9 3 7	75*	18	8 4 8	94*	31-	
6 0 10	515	502-	9 1 4	129*	47	8 2 13	51	51-	9 3 8	88	57	8 4 9	85*	48-	
6 0 12	325	379	9 1 5	129*	144	8 2 14	61*	49	9 3 9	64*	53	8 4 10	77*	31	
6 0 14	181*	149-	9 1 6	119*	25-	10 2 0	85*	60-	9 3 10	53*	22	10 4 0	55*	22	
6 0 16	92*	16-	9 1 7	119*	74-	10 2 1	12*	16-	9 3 11	37*	58-	10 4 1	60	63	
6 0 18	44	16-	10 2 2	3	1117	1123-	10 2 2	73*	20-	0 4 2	591	844-	10 4 2	55*	22
8 0 0	208*	164	10 2 3	3146	3047	10 2 3	73*	28-	0 4 3	806	817-	10 4 3	39*	19-	
8 0 2	316	223	0 2 4	2586	2524	10 2 4	4	73*	53	0 4 4	223	150-	10 4 4	28*	16-
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8 0 12	33*	16-	0 2 9	866	775	10 2 8	8	42*	21	0 4 8	478	255	1 5 3	297	359
8 0 14	109*	44	0 2 10	139*	133-	1 3 0	0	1446	1632-	0 4 9	863	971	1 5 4	612	655-
10 0 0	203	144	0 2 11	145	64	1 3 1	3	334	331	0 4 10	327	236-	1 5 5	251	225-
10 0 2	167	95-	0 2 12	145	27-	1 3 2	2	987	853	0 4 11	643	810-	1 5 6	790	788
10 0 4	127*	19-	0 2 13	151*	207	1 3 3	3	770	649	0 4 12	231	369	1 5 7	292	153
10 0 6	51*	16-	0 2 14	282	325-	1 3 4	4	393	434	0 4 13	500	617	1 5 8	201	147-
10 0 8	5*	16	0 2 15	236	307-	1 3 5	5	945	1042-	0 4 14	93	71-	1 5 9	320	181-
1 1 0	318	351	0 2 16	345	410	1 3 6	6	735	732-	0 4 15	77*	16-	1 5 10	292	329-
1 1 2	1263	1325	0 2 17	191	261	1 3 7	1038	1191	0 4 16	121*	36-	1 5 11	228	246	
1 1 3	871	908	0 2 18	194	240-	1 3 8	8	204	90	0 4 17	110*	36	1 5 12	329	285
1 1 4	787	811-	0 2 19	79	88-	1 3 9	9	268	120	0 4 18	94*	19-	1 5 13	155*	16-
1 1 5	1560	1699	0 2 20	94*	30	1 3 10	539	682	0 4 19	85*	24-	1 5 14	201*	25	
1 1 6	1298	1385	2 2 0	2822	3093-	1 3 11	212	118-	0 4 20	56*	16	1 5 15	192*	116	
1 1 7	763	682-	2 2 1	1647	1478-	1 3 12	427	381-	2 4 0	223	193	1 5 16	169*	129-	
1 1 8	672	593	2 2 2	2168	1564	1 3 13	110*	16	2 4 1	102*	119	1 5 17	71*	16	
1 1 9	560	563-	2 2 3	696	536	1 3 14	96	71	2 4 2	110*	47	1 5 18	128*	75	
1 1 10	210	129	2 2 4	536	389	1 3 15	220	182	2 4 3	899	945	1 5 19	740	742	
1 1 11	969	925	2 2 5	263	191-	1 3 16	188	101	2 4 4	665	635-	3 5 0	771	702	
1 1 12	168*	153-	2 2 6	7	133*	25	1 3 17	88	148-	2 4 5	1388	1578-	3 5 1	329	289-
1 1 13	350	336-	2 2 7	469	423-	1 3 18	133	89-	2 4 6	429	536	3 5 2	854	761-	
1 1 14	175*	157	2 2 8	366	448-	1 3 19	90*	80	2 4 7	1025	1033	3 5 3	329	352-	
1 1 15	224	94-	2 2 9	899	894	1 3 20	74*	41-	2 4 8	132*	170-	3 5 4	566	567	
1 1 16	164	196-	2 2 10	518	530	3 3 0	0	284	363-	2 4 9	327	308-	3 5 5	520	668
1 1 17	192	153	2 2 12	733	775-	3 3 1	1404	1573	2 4 10	137*	80	3 5 6	584	718-	
1 1 18	126	111	2 2 13	381	360-	3 3 2	586	538-	2 4 11	170	116-	3 5 7	219*	45-	
1 1 19	129*	27-	2 2 14	121	227	3 3 3	854	968-	2 4 12	137*	108	3 5 8	155	278	
1 1 20	109*	38-	2 2 15	145*	51-	3 3 4	1000	1122	2 4 13	132*	67-	3 5 9	274	231-	
3 1 0	1644	1751	2 2 16	139*	63	3 3 5	5	122*	118	2 4 14	159	73	3 5 10	269	325-
3 1 1	829	819-	2 2 17	91*	16	3 3 6	6	1239	1344-	2 4 15	195	251	3 5 11	301	238
3 1 2	1735	1858-	2 2 18	22*	16	3 3 7	284	270-	2 4 16	115	129-	3 5 12	306	194	
3 1 3	276	261-	2 2 19	23*	16	3 3 8	648	639	2 4 17	198	225-	3 5 13	123*	16	
3 1 4	808	783	2 2 20	85*	68-	3 3 9	9	523	578	2 4 18	85*	34	3 5 14	173	155-
3 1 5	1406	1598	4 2 0	1438	1421-	3 3 10	133*	45	2 4 19	77*	77	3 5 15	155*	110-	
3 1 6	832	936-	4 2 1	448	508-	3 3 11	671	786-	2 4 20	55*	24-	5 5 0	420	379	
3 1 7	1004	1083-	4 2 2	388	310	3 3 12	133*	18	4 4 0	132*	259	5 5 1	488	395-	
3 1 8	525	590	4 2 3	73*	16-	3 3 13	96	230	4 4 1	484	492	5 5 2	228	181-	
3 1 9	231	173-	4 2 4	318	359	3 3 14	127*	162-	4 4 2	132*	127*	5 5 3	374	327	
3 1 10	749	908-	4 2 5	578	557	3 3 15	88	191-	4 4 3	132*	132	5 5 4	164	250-	
3 1 11	479	369	4 2 6	606	642-	3 3 16	186	227	4 4 4	437	277	5 5 5	370	317*	
3 1 12	507	512	4 2 7	439	303-	3 3 18	141	146-	4 4 5	599	750-	5 5 6	297	391	
3 1 13	245	161-	4 2 8	33*	16-	3 3 19	74*	61-	4 4 6	283	249	5 5 7	241	155	
3 1 14</															



MU-18350

Fig. 1. Projection down the $[100]$ axis of half the unit cell of $\text{CBr}_4 \cdot \text{CH}_3\text{-C}_6\text{H}_4\text{-CH}_3$ showing the chain arrangement.



MU-18351

Fig. 2. Interatomic distances in $\text{CBr}_4 \cdot \text{CH}_3\text{-C}_6\text{H}_4\text{-CH}_3$.

The bromine atoms in only one of the 8 fold special positions of this space group (Br_1 in 8(f)) participate in the bonding within the zigzag chain. The distance to the central carbon atom is longer in this set of atoms than in the other set (8(g)). Thus, there is evidence of an interaction between the π electron system of the p-xylene molecule and one set of bromine atoms. This interaction is probably the reason for the existence of a compound. The stability of this compound can be attributed to this attractive force and the manner in which the molecules are packed in the crystal. The greater stability of the para isomer is presumably due to spatial requirements; it probably can pack more compactly than either the ortho or meta isomers.

The bonding in this compound seems to fall into the category of donor-acceptor interactions. Many examples of this general type have been reported in the literature (Andrews, 1954, p. 736). Of those of known crystal structure, the 1:1 benzene-bromine compound (Hassel and Strømme, 1958) is most closely analogous to the carbon tetrabromide p-xylene compound. In both compounds, each aromatic ring has a bromine atom on each side. The line joining these two neighbors is very nearly perpendicular to the plane of the ring and passes through its center. The distances from a bromine atom to the center of the ring 3.35\AA are the same for both compounds within experimental error.

THE CRYSTAL STRUCTURE OF PROPIONIC ACID

Introduction

Little work has been reported on the crystal structures of the low molecular weight monocarboxylic acids. While the few high molecular weight normal fatty acids of known structure are dimers (Vand, 1951; von Sydow, 1955), the lighter members of the series, formic and acetic acids, form long chain polymers in the solid (Holtzberg, Post, and Fankuchen, 1953; Jones and Templeton, 1958). Finding a chain structure for solid acetic acid raised the question of whether the chain structure was common to all the low molecular weight fatty acids.

When the number of carbon atoms per molecule of acid is plotted versus the melting point, the points fall on two rather similar curves, one for odd, the other for even numbers of carbon atoms. The interesting feature is that both curves reach a minimum in the vicinity of five carbon atoms per molecule. Two different melting points have been reported for n-valeric acid, one falling on the curve for the even and the other on the curve for the odd number of carbon atoms per molecule. From this fact, it would almost be expected that valeric acid is the transition point between the dimer fatty acid structure and the chain structure. Such is not the case; this investigation showed that the dimer structure occurs in propionic acid. This result is not unreasonable upon considering how an increase in the length of the carbon chain would affect the packing of the molecules in the unit cell.

Experimental Procedure

The x-ray experiments were made 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. This was accomplished by boiling nitrogen from a 100 liter Dewar flask through a series of glass Dewar tubes connected by semiflexible insulated joints to a Dewar tube coaxial with, and inside of, the layer line screen of the camera (Krueger, 1955). By varying the current in a resistor placed in the Dewar flask of nitrogen, the rate of flow of cold gas was

changed so as to produce the desired temperature. The temperature was measured by means of a copper-constantan thermocouple placed in the cooling stream 0.5 cm from the end of the capillary.

A sample of propionic acid ($\text{CH}_3\text{-CH}_2\text{-COOH}$) was cooled to the vicinity of the melting point. The melting point as determined in the experiment (-20.5°C), is in good agreement with that reported in the literature, -20.7°C (Timmermans, 1952). While the temperature at the thermocouple was kept just below the melting point of the acid, a single crystal was obtained by touching the capillary with the finger until all but one very small single crystal had melted. The seed crystal was then allowed to grow. The growth and decay of the crystal was followed through a polarizing microscope. After several attempts, a satisfactory cylindrical single crystal, 5 mm long and 0.3 mm in diameter, was obtained. The crystal was lined up about the a axis and preliminary oscillation photographs were taken at -67°C . Rotation and zero-through third-level multiple-film Weissenberg photographs were taken at $-95 \pm 2^\circ\text{C}$, with $\text{CuK}\alpha$ radiation ($\text{CuK}\alpha_1$; $\lambda = 1.54050 \text{ \AA}$). After the complete set of Weissenberg photographs was made, another zero level exposure was taken. This one was calibrated by superimposing on it a zero layer strip of the c -axis rotation pattern of alpha quartz ($a = 4.913 \text{ \AA}$).

Space Group and Unit Cell

The calculated density of propionic acid at -95°C , assuming four molecules per unit cell, is 1.234 g cm^{-3} . The reported density of propionic acid at -35°C is 1.1894 g cm^{-3} (Rozenal, 1936).

The photographs of propionic acid exhibited Laue symmetry $2/m$. The extinctions present ($h0\ell$ with $\ell = 2n + 1$ and $0k0$ with $k = 2n + 1$) indicated space group $\text{P}2_1/c$ (C_{2h}^5) as the most likely. Since the extinctions present may not be caused by symmetry conditions, but may rather be due to special arrangement of the atoms (Templeton, 1956), space groups $\text{P}2$, $\text{P}2_1$, Pm , $\text{P}2/m$, $\text{P}2_1/m$ and especially Pc and $\text{P}2/c$ cannot be ruled out immediately. However, the subsequent refinement using the fourfold general positions,

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

of space group $\text{P}2_1/c$ confirmed this choice.

Since the crystals always grew with the a axis parallel to the capillary axis, it was impossible to align a crystal about any other axis. The unit cell dimensions were determined from a quartz calibrated Weissenberg photograph about the a axis and an uncalibrated rotation photograph. The monoclinic angle, β , was determined by the method of angular lag (Buerger, 1942, p. 377) using all three higher level Weissenberg photographs. The cell dimensions are $a = 4.042 \pm 0.040$, $b = 9.063 \pm 0.010$, $c = 10.998 \pm 0.010 \text{ \AA}$ and $\beta = 91^{\circ} 15' \pm 8'$.

Determination of the Structure

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. Throughout the least squares refinements a weighting scheme similar to that of Hughes (1941) was used. The weights for the observed reflections were taken as $(F_{\text{obs}})^{-2}$ or as $(4F_{\text{min}})^{-2}$ if the uncorrected intensity was less than four times the minimum observed intensity. For the reflections too weak to be observed, F_{obs} was set equal to F_{min} , and if $|F_{\text{min}}| \geq |F_{\text{calc}}|$, the weight was taken as zero and $|F_{\text{min}}| - |F_{\text{calc}}|$ set equal to zero; otherwise, the weight was taken as $(4F_{\text{min}})^{-2}$ and $|F_{\text{min}}| - |F_{\text{calc}}|$ set equal to $-|F_{\text{calc}}|$.

Most of the least squares refinements were carried out using the diagonal approximation least squares program of Senko and Templeton (Senko, 1957). The last few cycles were run by using a modification of the program similar to that described by Hardgrove (Hardgrove, 1959), which used the complete least squares matrix.

There was a total of 743 independent reflections in the portion of reciprocal space investigated. The intensities of the 603 observed reflections (140 unobserved) were estimated visually by multiple-film techniques. The intensities ranged from 1 to 16,000. They were corrected for the Lorentz, polarization, and velocity effects by an IBM 650 routine, INCOR. No correction was made for absorption since μ_r for this crystal was 0.15.

By using the corrected intensities of the observed reflections and scaling the four levels according to the exposure time, a three dimensional Patterson synthesis was calculated with the IBM 701 Fourier program (Dodge, 1958). The resolution was not good, and it was thought that a sharpened Patterson function might give better resolution of the atomic vectors. Consequently, the coefficients were modified by the factor $[\exp(-0.9 \sin^2 \theta) (12f_C + 8f_O)]^{-1}$, and these modified coefficients were used to calculate the sharpened Patterson synthesis.

There was some improvement in the degree of resolution, especially in the Harker section at $y = 1/2$. At other sections the increase in resolution was not as great as was hoped for. An interpretation of the sharpened Patterson synthesis yielded the following coordinates.

	<u>x</u>	<u>y</u>	<u>z</u>
Oxygen 1	0.975	0.41	0.57
Oxygen 2	-	-	-
Carbon 3	0.25	0.41	0.75
Carbon 4	0.37	0.32	0.83
Carbon 5	0.15	0.32	0.67

These coordinates showed a preference for the dimer structure although no such assumption was made when the Patterson synthesis was interpreted.

With these approximate coordinates, three dimensional Fourier refinements were attempted but with no success. Various modifications of this structure based on the Fourier results were also used but no improvement in agreement was noted. Throughout all these trials the unreliability factor, R_1 , ranged from 0.50 to 0.55.

Both the chain and dimer structures still remained as possibilities. However, from spatial considerations, the dimer structure seemed more probable. A new trial structure was obtained by assuming the dimer structure, placing it about a center of symmetry, and using the information about the x and z coordinates obtained from the Harker section at $y = 1/2$.

	<u>x</u>	<u>y</u>	<u>z</u>
O ₁	0.97	0.32	0.565
O ₂	0.23	0.53	0.63
C ₃	0.25	0.32	0.75
C ₄	0.38	0.40	0.845
C ₅	0.18	0.40	0.65

Structure factors for the observed $0kl$ data were calculated by using these coordinates and gave an R_1 of .365.

Two cycles of least squares refinement on the zero layer brought R_1 down to 0.190. At this point full three dimensional refinements of the observed reflections were begun. The first cycle of three dimensional refinement gave an R_1 of 0.267. After the fourth cycle R_1 was 0.159, but when the unobserved reflections were added, $R_1 = 0.169$. After three more cycles $R_1 = 0.164$. Since R_1 was decreasing so slowly, it was thought that the addition of the hydrogen coordinates would improve the agreement. Hydrogen positions were calculated by assuming a C-H bond length of 1.08Å, tetrahedral angles about the carbon atoms, and a staggered configuration for the hydrogen atoms of the methyl group relative to the substituents on the α -carbon atom. The addition of the hydrogen atom coordinates to the structure factor calculation decreased R_1 to 0.151. However, certain obvious discrepancies between observed and calculated structure factors were noted. The data were rechecked to eliminate any mistakes and five very strong reflections (011, 021, 024, 11 $\bar{1}$, 11 $\bar{2}$) which were thought to suffer from extinction were removed from the least squares calculations. The refinements were continued, and after two more cycles of least squares refinement $R_1 = 0.116$. The removal of the five reflections from the calculations thus improved the progress of the refinement considerably. The large discrepancy in $|F_o| - |F_c|$ because of these five reflections controlled the scale factor, and removal of these reflections allowed a normal distribution of positive and negative values of $|F_o| - |F_c|$.

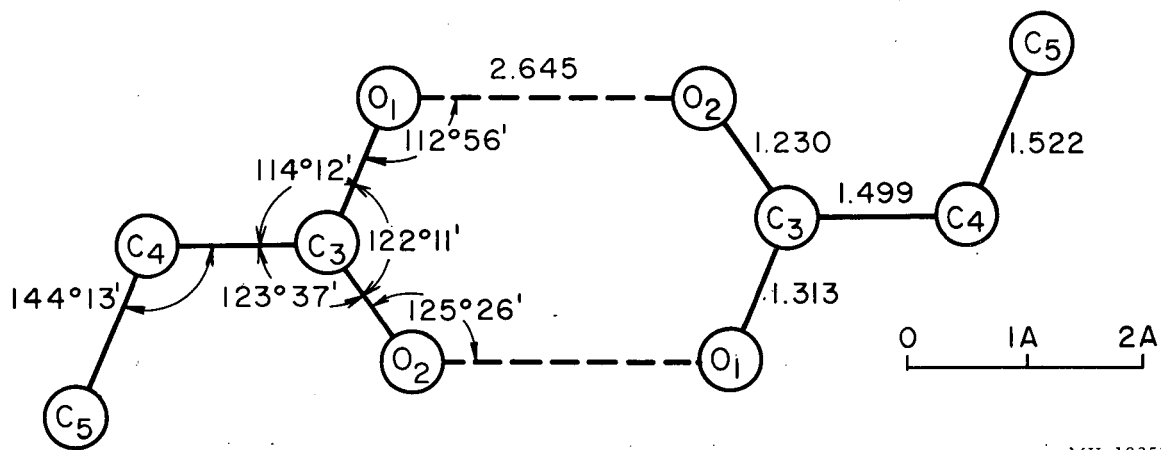
The final diagonal approximation least squares parameters, standard deviations, and bond lengths are listed in Table IV. A drawing of dimeric molecule is shown in Fig. 3.

Table IV

Final diagonal approximation least squares parameters							
	<u>x</u>	<u>y</u>	<u>z</u>	<u>B</u>	<u>σ_x</u>	<u>σ_y</u>	<u>σ_z</u>
O ₁	-.0225	.3196	.5679	2.93	.0009	.0004	.0003
O ₂	.2225	.5289	.6258	2.76	.0009	.0004	.0003
C ₃	.1558	.3988	.6452	2.25	.0012	.0005	.0004
C ₄	.2715	.3164	.7559	2.69	.0013	.0005	.0004
C ₅	.4126	.4139	.8570	3.22	.0014	.0006	.0005
H ₆	-.105	.379	.488	3.56	assumed		
H ₇	.078	.256	.790	3.56	assumed		
H ₈	.454	.247	.729	3.56	assumed		
H ₉	.499	.356	.937	3.56	assumed		
H ₁₀	.579	.481	.828	3.56	assumed		
H ₁₁	.253	.486	.880	3.56	assumed		
R ₁ = .115		R ₂ = .113		R ₃ = .118		for 738 reflections	

Bond lengths

O ₁ - O ₂	2.641±.005Å
O ₁ - C ₃	1.310±.006Å
O ₂ - C ₃	1.229±.006Å
C ₃ - C ₄	1.492±.006Å
C ₄ - C ₅	1.517±.006Å



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Fig. 3. Distances and angles in propionic acid.

Because of the interest in the difference between diagonal-approximation and full-matrix least-squares calculations, and also in order to get an idea of the magnitude of the cross terms and the correlation coefficients, several cycles of full-matrix refinements were run. The resulting parameters, standard deviations, and bond lengths after the second full-matrix cycle are listed in Table V. The observed and calculated structure factors for these parameters are listed in Table VI. The inverted A matrix is listed in Table VII.

Discussion of the Structure

The structure consists of dimers of propionic acid about the center of symmetry (see Fig. 4). All the heavy atoms of a dimer except the terminal carbon (C_5) are planar within experimental error ($.009\text{\AA}$). The methyl carbon is $.284\text{\AA}$ out of the plane, and forms an angle of $10^\circ 45'$ with the plane, which is given by the equation $-.21702 x + .07039 y + .12438 z = 1$, where x , y , and z (in angstroms) are measured along the a , b , and c axes.

The methyl group is trans with respect to the hydroxyl oxygen atom. The two propionic acid molecules are connected by hydrogen bonds 2.645\AA long. The carbon-oxygen bonds of 1.230\AA and 1.313\AA are in accord with those of formic and acetic acid. Although the carbon-carbon bonds are shorter than 1.54\AA , the departure from this length is not unexpected. Some recent determinations of pure hydrocarbon bond lengths have shown the C-C bond to be about $.01\text{\AA}$ shorter than in diamond (Bartell, 1959; Shearer and Vand, 1956).

The carbon atom bonded to the oxygen atom does not have tetrahedral bonding. Thus, one would expect that there would be some deviation from the sp^3 bond length. The distance 1.50\AA corresponds to about 10% double bond character according to Pauling (Pauling, 1942). Since this double bondedness of the one C-C bond could also be expected to shorten the other C-C bond the 1.52\AA length is very reasonable inasmuch as it corresponds to about 3% double bondedness on the Pauling scale.

Table V

Parameters after full matrix least squares refinements								
	<u>x</u>	<u>y</u>	<u>z</u>	<u>B</u>	<u>σ_x</u>	<u>σ_y</u>	<u>σ_z</u>	<u>σ_B</u>
O ₁	-.0221	.3196	.5679	2.96	.0009	.0004	.0003	.08
O ₂	.2222	.5291	.6258	2.77	.0009	.0004	.0003	.08
C ₃	.1554	.3988	.6450	2.27	.0012	.0005	.0004	.08
C ₄	.2717	.3162	.7560	2.72	.0013	.0005	.0004	.09
C ₅	.4127	.4138	.8571	3.25	.0014	.0006	.0005	.10
H ₆	-.105	.379	.488	3.56	assumed			
H ₇	.078	.256	.790	3.56	assumed			
H ₈	.445	.247	.729	3.56	assumed			
H ₉	.499	.356	.937	3.56	assumed			
H ₁₀	.579	.481	.828	3.56	assumed			
H ₁₁	.253	.486	.880	3.56	assumed			
$R_1 = .116$			$R_2 = .113$		$R_3 = .118$ for 738 reflections			

Bond lengths

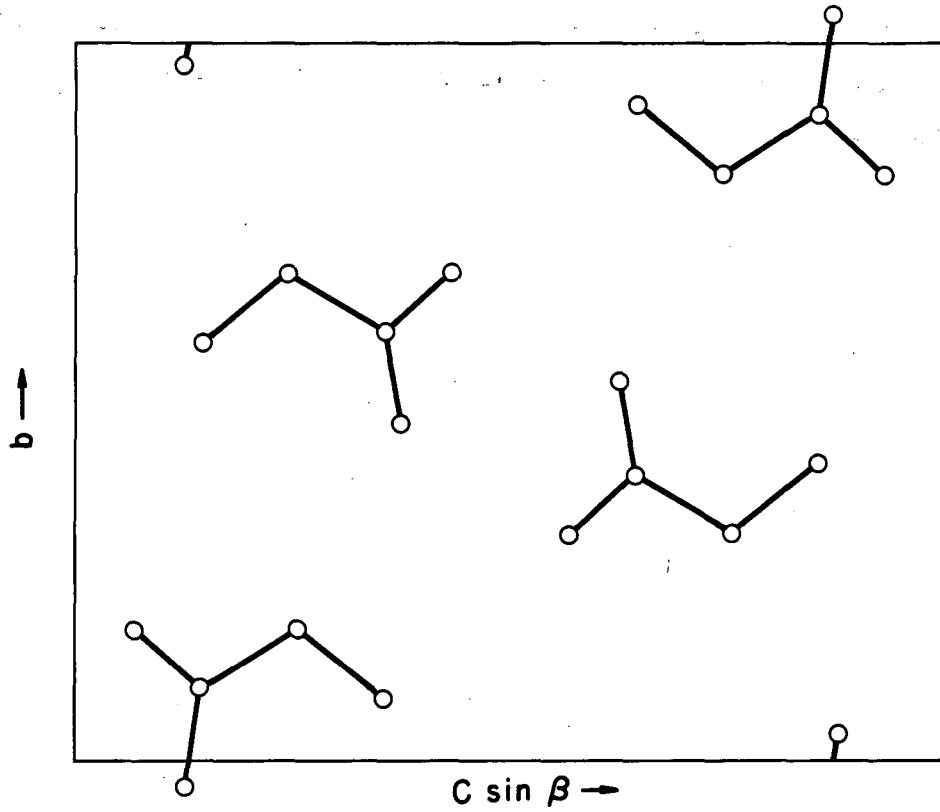
O ₁ - O ₂	2.645±.005 Å
O ₁ - C ₃	1.313±.007 Å
O ₂ - C ₃	1.230±.006 Å
C ₃ - C ₄	1.499±.006 Å
C ₄ - C ₅	1.522±.006 Å

Table VI. Observed and calculated structure factors for propionic acid. * indicates minimum observable structure factor. ** indicates intensity measurement very uncertain. These ** reflections were omitted from the least-square and Fourier calculations.

Table with 16 columns: h, k, l, F_o, |F_c|, h, k, l, F_o, |F_c|, h, k, l, F_o, |F_c|, h, k, l, F_o, |F_c|. It contains a grid of numerical data points representing structure factors for various hkl reflections.

Table VII
 A portion of the A^{-1} matrix of propionic acid
 (All values are $\times 10^5$)

	<u>K</u>	<u>x₁</u>	<u>x₂</u>	<u>x₃</u>	<u>x₄</u>	<u>x₅</u>	<u>y₁</u>	<u>y₂</u>	<u>y₃</u>	<u>y₄</u>	<u>y₅</u>	<u>z₁</u>	<u>z₂</u>	<u>z₃</u>	<u>z₄</u>	<u>z₅</u>	<u>B₁</u>	<u>B₂</u>	<u>B₃</u>	<u>B₄</u>	<u>B₅</u>
K	214.45	-.76	-.67	-1.15	-1.15	-1.14	.01	-.16	.04	-.36	-.22	-.37	-.30	.42	.19	.26	520.38	497.04	405.74	449.65	470.55
x ₁		2.20	.04	.04	.10	-.13	0	0	.03	0	0	.03	.01	.04	.01	0	-2.10	-12.43	-.65	-1.60	-2.74
x ₂			2.18	-.06	.10	-.07	0	0	.02	0	-.01	.01	.03	-.01	0	-.01	-1.49	-1.19	-2.72	-1.98	-2.86
x ₃				4.14	-.07	-.03	.03	.03	0	.03	0	.05	-.01	.04	.04	0	-1.94	-1.34	-2.30	-2.67	-4.86
x ₄					4.70	.09	-.01	0	-.03	0	.05	.01	0	.04	.07	.06	-2.87	-2.23	-3.16	-3.85	-1.47
x ₅						5.67	0	.02	.02	.06	0	0	-.01	0	.06	.06	-3.56	-4.05	-3.07	-1.20	-4.19
y ₁							.39	0	0	0	0	0	0	0	0	0	0	-.03	.02	-.11	.18
y ₂								.36	.02	.01	0	0	0	0	0	0	-.55	-.29	-.70	-.14	-.08
y ₃									.63	.01	-.01	.01	0	0	-.01	0	-.44	.21	.02	.15	.62
y ₄										.74	.01	0	0	0	0	.02	-1.09	-.89	-.92	-.74	-.60
y ₅											.93	0	0	-.01	.02	.01	-.14	-.66	-.81	-1.06	-.47
z ₁												.25	0	.01	0	0	-.96	-.61	-.27	-.90	-.96
z ₂													.23	-.02	0	0	-.54	-.68	.43	-.58	-.77
z ₃														.41	.02	.01	.76	.10	.70	1.14	.18
z ₄															.49	.02	.38	.41	.16	-.22	.27
z ₅																.59	.35	.15	.32	.31	.60
B ₁																	3088.82	1205.86	963.96	1077.73	1149.19
B ₂																		2846.45	891.71	1041.78	1070.84
B ₃																			3327.95	909.51	847.10
B ₄																				4120.97	1072.15
B ₅																					5152.27



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Fig. 4. A projection along $[100]$ of the unit cell of propionic acid.

Varying distances for bonds comparable to those in propionic acid are reported in the literature. Selected values are listed in Table VIII. The bond lengths and angles obtained in this determination are in good agreement with all other determinations and have a smaller standard deviation than the majority of the previous determinations.

Table VIII

Selected bond distances (all distances in Å)										
Compound	Method	C-O	C=O	O-H...O	C-C _a	C-C _{aβ}	C _β -C _γ	C _γ -C _δ	C _δ -C _ε	Reference Page
Diamond	x-Ray				1.54452 ±.00014					1 M102
Formaldehyde	I-R + U. V.		1.230±.017							1 M109
Formic acid	x-Ray	1.26	1.23	2.58						1 M109
Formic acid	Microwave	1.312	1.245							1 M109
Formic acid	Electron diffraction	1.36±.01	1.23±.01							1 M109
Oxalic acid	x-Ray	1.29±.01	1.19±.01		1.56±.01					1 M125
Oxalic acid dihydrate	x-Ray	1.29±.01	1.19±.02		1.53±.02					1 M125
Formic acid dimer	Electron diffraction	1.36±.04	1.25±.03	2.73±.05						1 M133
Acetic acid	Electron diffraction	1.43±.03	1.24±.03	2.76±.06	1.54±.04					1 M132
Acetic acid	x-Ray	1.29±.02	1.24±.02	2.61±.02	1.54±.02					2 484
Sodium oxalate	x-Ray	1.23±.03	1.23±.03		1.54±.03					1 M142
Ammonium oxalate	x-Ray	1.25±.02	1.23±.02		1.56±.02					1 M142
β-nitro propionic acid	x-Ray	1.34±.03	1.22±.03	2.66±.03	1.56±.03	1.53±.03				1 M149
Methyl acetate	Electron diffraction	1.36±.04	1.22±.03		1.52±.04					1 M151
Maleic acid	x-Ray	1.28, 1.28	1.20, 1.21	2.46	1.44 1.47	1.43				1 M163
Succinic acid	x-Ray	1.30	1.25		1.51	1.50				1 M166
Dimethyl oxalate	x-Ray	1.31±.03	1.19±.03		1.53±.03					1 M167
β-glutaric acid	x-Ray	1.30	1.23	2.69	1.53	1.53				1 M184
Adipic acid	x-Ray	1.29	1.23		1.52	1.49	1.54			1 M203
Benzoic acid	x-Ray	1.29±.014	1.24±.014	2.64±.02	1.48±.016					1 M212
Pimelic acid	x-Ray	1.38	1.28		1.44	1.49	1.50			1 M214
Sebacic acid	x-Ray	1.27	1.24		1.51	1.48	1.53	1.50	1.54	1 M226
Malonic acid	x-Ray	1.29	1.24	2.71	1.52					3 125
Pimelic acid	x-Ray	1.31	1.22	2.68	1.54					
		1.34	1.20	2.67	1.50	1.52	1.55			4 289
		1.26	1.24	2.68	1.48	1.52	1.56			

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THE CRYSTAL STRUCTURE OF n-BUTYRIC ACID

Introduction

In the determination of the structure of propionic acid, carbon-carbon bonds less than 1.54\AA long were found. This raised the question of whether this was an isolated case or whether the same feature would occur in the succeeding members of the series. The logical choice for continuing the investigation of bond lengths and crystal structure was n-butyric acid, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-COOH}$.

Experimental Procedure

A small quantity of n-butyric acid was sealed in a glass capillary 0.3 mm in diameter and mounted on the goniometer head of a specially modified low-temperature Weissenberg camera (Olovsson and Templeton, 1959). A single crystal was grown in the usual manner and aligned about the a axis by means of oscillation photographs.

The melting point of this butyric acid sample (about -7°C) was not entirely in accord with the literature value of -5.5°C (Timmermans, 1950, p. 387). This discrepancy must be partially attributed to the difficulty of measuring the temperature exactly at the crystal. In order to get a temperature of -5°C , a very low rate of flow of cooling gas was used. Thus, there could have been appreciable heating between the point at which the thermocouple was inserted in the gas stream and the crystal itself.

A rotation picture was taken at a temperature of $-43 \pm 2^\circ\text{C}$ and also multiple-film zero - through sixth-layer Weissenberg photographs. CuK α radiation ($\lambda = 1.5418\text{\AA}$) was used. Although preliminary examinations of a butyric acid crystal indicated a phase transition in the vicinity of -55°C , no structure determination was made at lower temperatures since the crystal available seemed to be twinned and fragmented at these lower temperatures.

Unit Cell and Space Group

The Weissenberg pictures exhibited Laue symmetry, $2/m$. The systematic absences indicated a C-centered lattice. The probable space groups were $C2/m(C_{2h}^3)$, $C2(C_2^3)$, and $Cm(C_s^3)$. If this acid were to have a dimer structure similar to propionic acid, the centric space group would be preferred. A satisfactory refinement was carried out by using $C2/m$, which tends to confirm this choice.

The unit cell dimensions were determined from a calibrated zero-layer Weissenberg photograph, and uncalibrated rotation and higher-layer Weissenberg pictures. The zero-layer Weissenberg picture was not calibrated directly with a quartz pattern, but with the rotation pattern of the butyric acid crystal at -195°C . It had been hoped that information could be gathered about the low temperature form, and it was impossible to preserve the crystal and still make a quartz calibration. The low-temperature zero-layer Weissenberg photograph was in turn calibrated with a zero layer strip of the rotation pattern of α -quartz ($a = 4.913$). The monoclinic angle β was determined by the method of angular lag (Buerger, 1942, p. 377). The unit cell dimensions are $a = 8.014 \pm 0.080$, $b = 6.815 \pm 0.020$, $c = 10.145 \pm 0.030 \text{ \AA}$, and $\beta = 111^\circ 27' \pm 15'$. The calculated density based on four molecules per unit cell is 1.135 g cm^{-3} . This is in agreement with the reported density of 1.0875 g cm^{-3} at -12°C (Rozenal, 1936).

Structure Determination

The atomic scattering factors of Hoerni and Ibers (1954) for carbon and oxygen and of the Internationale Tabellen (1935) for hydrogen were used in all structure factor calculations. The diagonal-approximation least-squares program of Senko and Templeton (Senko, 1957) was used for the least-squares refinements. In all the refinements, the weights of the observed reflection were taken as $(F_{\text{obs}})^{-2}$ or $(4F_{\text{min}})^{-2}$ if the uncorrected intensity was less than four times the minimum observed intensity. When the reflections were too weak to be observed, F_{obs} was set equal to F_{min} . For $|F_{\text{min}}| \geq |F_{\text{calc}}|$, the weight was taken as zero, and $|F_{\text{obs}}| - |F_{\text{calc}}|$ was set equal to zero. For $|F_{\text{min}}| < |F_{\text{calc}}|$, the reflection was treated in the same manner as an observed reflection.

The intensities of the various reflections were estimated visually by comparison with a standard film strip. A total of 353 observed and 84 unobserved reflections occurred in the portion of reciprocal space photographed by the seven Weissenberg levels. The routine intensity corrections were made with the INCOR IBM 650 routine. No correction for absorption was deemed necessary since $\mu r < 0.15$.

A three-dimensional Patterson synthesis was calculated with the corrected intensities and also a sharpened Patterson synthesis in which the coefficients were modified by the factor $[(8f_O + 16f_C) \exp(-0.9 \sin^2 \theta)]^{-1}$. There was not a great deal of differences between the two functions although the resolution of peaks was somewhat greater in the sharpened Patterson synthesis.

The synthesis did show, however, an almost total concentration of peaks in the sections $y = 0$ and $y = 1/2$. This indicated that the molecules lie in a plane perpendicular to the b axis, one-half a cell apart. A trial structure consistent with the Patterson function was found by assuming a dimer structure about a center of symmetry, and placing the molecules in the mirror plane special positions of space group $C2/m$,

$$4 (i): \pm(x, 0, z) + C.$$

The coordinates were the following.

	<u>x</u>	<u>y</u>	<u>z</u>
O ₁	0.22	0	0.03
O ₂	0	0	0.83
C ₃	0.16	0	0.90
C ₄	0.29	0	0.82
C ₅	0.20	0	0.66
C ₆	0.34	0	0.60

Successive least-squares refinements brought the discrepancy factor, R_1 , down to 0.167. Hydrogen atoms were added to the calculation by assuming a staggered configuration of the hydrogen atoms in the chain. The hydrogen atom in the hydrogen bond was placed on the line between the oxygen atoms, 1.6\AA away from the carbonyl oxygen.

This placed them in two sets of general positions,

$$8(j) : \pm(x, y, z, \pm x, \bar{y}, z) + C,$$

and two sets of special positions, 4 (i).

Further refinement gave an R_1 of 0.128. However, the positions of the hydrogen atoms were very unreliable, and in the final calculation the hydrogen parameters were left out. The final R_1 of 0.159 is based only on the carbon and oxygen parameters. These are listed in Table IX together with their standard deviations and bond lengths. A drawing of the dimeric molecule is shown in Fig. 5. The observed and calculated structure factors for the final carbon and oxygen parameters are listed in Table X. It is hoped that further refinement can be carried out using anisotropic temperature factors, and that this will improve the accuracy of the structure.

Discussion of the Structure

The structure as reported has all the carbon and oxygen atoms located in a mirror plane, about a center of symmetry. This gives a planar dimer structure. However, a three-dimensional difference synthesis showed that there are fairly large anisotropic thermal vibrations. This anisotropic motion may account for the fairly large value of the discrepancy factor, R_1 , and the short terminal C-C bond.

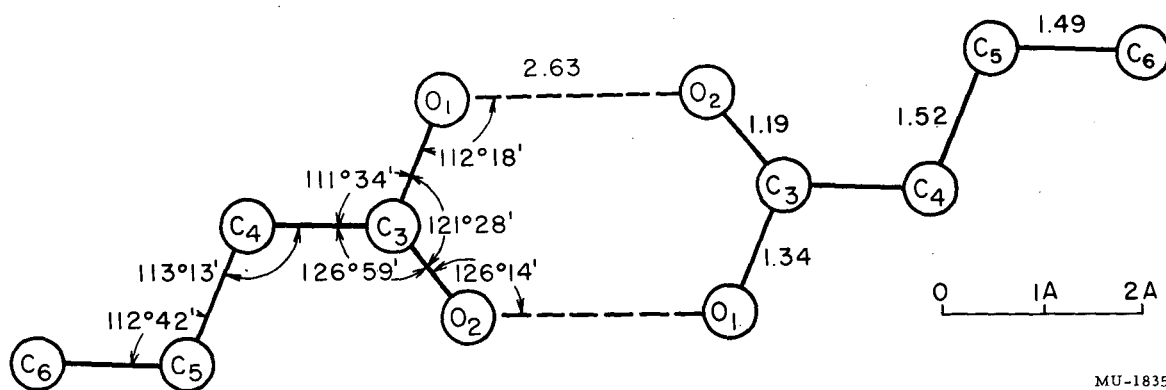
Except for this short terminal C-C bond, the lengths are in agreement with those observed in propionic acid. It is surprising that the butyric acid molecule is planar when the propionic acid molecule has the terminal carbon atom out of plane. The accuracy of the bond lengths is affected by the anisotropic vibration and is not as great as had been desired. However, it does appear that there is a significant departure from the 1.54\AA C-C bond length in the low molecular weight fatty acids.

Table IX

Final parameters for butyric acid							
	<u>x</u>	<u>y</u>	<u>z</u>	<u>B</u>	<u>σ_x</u>	<u>σ_y</u>	<u>σ_z</u>
O ₁	.2365	0	.0370	8.19	.0011	-	.0008
O ₂	-.0008	0	.8377	7.49	.0010	-	.0007
C ₃	.1580	0	.8951	6.51	.0014	-	.0010
C ₄	.2919	0	.8267	7.54	.0016	-	.0012
C ₅	.2082	0	.6654	8.86	.0018	-	.0013
C ₆	.3452	0	.5975	8.89	.0018	-	.0013
$R_1 = .159$ $R_2 = .154$ $R_3 = .154$ for all 437 reflections							

Bond distances

O ₁ - O ₂	2.63±.02 Å
O ₁ - C ₃	1.34±.01 Å
O ₂ - C ₃	1.19±.02 Å
C ₃ - C ₄	1.48±.02 Å
C ₄ - C ₅	1.52±.02 Å
C ₅ - C ₆	1.49±.02 Å



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Fig. 5. Distances and angles in n-butyric acid.

Table X. Observed and calculated structure factors for n-butyric acid. * indicates minimum observable structure factor. ** indicates intensity measurement very uncertain. These ** reflections were omitted from the least-squares and Fourier calculations.

Table with 5 columns of data: h k l, F_o, |F_c|, h k l, F_o, |F_c|, h k l, F_o, |F_c|, h k l, F_o, |F_c|. The table lists observed and calculated structure factors for various reflections of n-butyric acid, including intensity measurements and calculated values.

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