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The Crystal Structure of Valeric Acid

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A three dimensional X-ray study of crystalline valeric acid has shown it to be monoclinic with

$$a = 5{\cdot}55,\ b = 9{\cdot}664,\ c = 11{\cdot}341\ \text{Å};\ \beta = 101°\ 49',;\ Z = 4,$$

and space group C_5^{2h}–$P2_1/c$. The trial structure was obtained from a Patterson function of the *a* axis projection. The structure was refined by least-squares methods. The final structure consists of dimers located about a center of symmetry with a hydrogen bond distance of 2·63 Å. The observed interatomic distances are C–O = 1·35, 1·26 Å; C–C = 1·53, 1·53, 1·57, 1·57 Å. All intermolecular contact distances are normal.

Introduction

Recent studies of the crystal structures of formic acid (Holtzberg, Post & Fankuchen, 1953), acetic acid (Jones & Templeton, 1958), propionic acid (Strieter, Templeton, Scheuerman & Sass, 1962) and butyric acid (Strieter & Templeton, 1962) show that the molecular packings of these fatty acids are quite varied. The fact that the melting point of valeric acid ($CH_3CH_2CH_2CH_2COOH$) is lower than that of any other normal fatty acid suggests that either the crystal structure is also of a different nature or that the properties of the liquid state of these acids are largely responsible for their melting behavior. This paper describes the crystal structure of valeric acid as determined by X-ray diffraction. The crystal was found to consist of hydrogen bonded dimers with a molecular packing quite similar to that of propionic acid.

Experimental

Preparation of crystals

Attempts to obtain single crystals of valeric acid using the technique described for propionic acid (Strieter, Templeton, Scheuerman & Sass, 1962) were unsuccessful. However, a much simpler method was devised by which satisfactory single crystals could be obtained in less than an hour's time. Several milliliters of valeric acid were placed in a 30 ml. pear shaped flask. The flask was then placed in a beaker filled with glass beads and the entire assembly set in a Dewar flask filled with crushed dry ice. Under these conditions the valeric acid slowly freezes into well formed crystals. The crystals were broken free from the flask and shaken onto a metal plate cooled by a large block of dry ice. Several small needle-like crystals were selected and placed in 0·3 mm. glass capillaries. A capillary was glued in a brass pin while

Table 1. *Valeric acid atomic parameters*

	Final (isotropic temp. factors)				Final (anisotropic temp. factors)		
Atom	*x*	*y*	*z*	*B*	*x*	*y*	*z*
C_5	0·8162	0·4544	0·1121	5·565	0·8196	0·4553	0·1136
C_4	0·6620	0·3567	0·1817	4·561	0·6607	0·3582	0·1805
C_3	0·5163	0·4428	0·2619	3·678	0·5174	0·4414	0·2628
C_2	0·3857	0·3390	0·3322	3·976	0·3862	0·3400	0·3324
C_1	0·2293	0·4116	0·4066	3·974	0·2208	0·4112	0·4065
O_2	0·1983	0·5405	0·4146	4·593	0·1957	0·5403	0·4146
O_1	0·0971	0·3267	0·4700	4·540	0·0978	0·3280	0·4689

Table 2. *Valeric acid final observed and calculated structure factors*

0 k l	$\lvert F_o \rvert$	F_c
0 12	6.59	6.97
0 10	3.74	4.07
0 8	3.58	- 2.42
0 6	13.15	-12.58
0 4	15.36	-15.74
0 2	2.96	7.27
1 13	5.50	5.51
1 12	< 1.88	.01
1 11	< 2.10	2.84
1 10	3.72	3.37
1 9	< 2.07	.94
1 8	6.93	7.75
1 7	11.18	-13.99
1 6	9.20	9.79
1 5	8.74	- 8.67
1 4	10.85	10.66
1 3	13.74	11.80
1 2	10.85	11.07
1 1	39.02	40.07
2 13	5.48	5.73
2 12	3.64	3.05
2 11	< 2.05	1.10
2 10	4.94	5.46
2 9	3.09	3.49
2 8	3.05	6.50
2 7	7.83	9.22
2 6	26.87	-29.25
2 5	< 1.48	.04
2 4	18.93	-18.53
2 3	6.41	5.78
2 2	3.01	- 4.37
2 1	68.90	58.27
2 0	43.13	35.92
3 13	1.97	2.20
3 12	2.85	- 1.80
3 11	3.54	3.38
3 10	< 2.12	2.45
3 9	< 2.12	2.46
3 8	< 2.04	- 2.42
3 7	11.28	-12.00
3 6	2.58	2.63
3 5	9.65	- 8.76
3 4	6.52	- 6.17
3 3	14.12	-12.37
3 2	16.75	-12.94
3 1	23.63	-18.38
4 12	2.30	- 2.20
4 11	< 1.92	1.66
4 10	< 2.09	.21
4 9	< 2.14	2.00
4 8	4.56	5.54
4 7	19.78	-21.47
4 6	13.51	-12.95
4 5	< 1.71	- 2.34
4 4	3.27	- 3.33
4 3	16.78	-16.00
4 2	< 1.37	3.84
4 1	5.70	.47
4 0	12.56	-18.03
5 12	2.16	- 2.17
5 11	< 1.79	- .99
5 10	< 2.00	1.23
5 9	4.74	- 4.70
5 8	3.19	- 3.01
5 7	3.16	3.06
5 6	4.00	2.30
5 5	6.89	7.70
5 4	18.71	-19.21
5 3	5.50	4.88
5 2	22.48	-20.99
5 1	9.69	7.92
6 11	2.37	2.86
6 10	2.78	- 3.32
6 9	8.77	9.56
6 8	5.88	- 4.81
6 7	5.50	- 4.67
6 6	17.60	16.85
6 5	4.77	2.69
6 4	4.48	5.04
6 3	10.53	-10.65
6 2	6.31	6.51
6 1	3.54	- 2.46
6 0	14.48	10.53
7 10	2.79	4.12
7 9	< 1.88	- 1.88
7 8	12.72	12.42
7 7	7.04	6.49
7 6	10.01	9.92
7 5	< 2.10	1.32
7 4	8.21	- 8.54
7 3	3.43	4.70
7 2	8.76	- 8.97
7 1	< 1.94	- 1.71
8 9	5.17	7.23
8 8	4.59	- 3.56
8 7	10.12	1.00
8 6	8.17	7.37
8 5	5.73	- 4.54
8 4	3.09	- 3.05
8 3	8.02	- 8.71
8 2	5.03	- 3.71
8 1	3.07	3.67
8 0	14.66	-16.95
9 9	1.79	1.40
9 8	4.03	4.72
9 7	< 1.77	.59
9 6	< 1.91	.01
9 5	4.77	- 5.16
9 4	5.42	- 5.27
9 3	< 2.12	- 2.42
9 2	11.30	-12.12
9 1	7.73	- 8.24

0 k l	$\lvert F_o \rvert$	F_c
10 5	5.74	- 5.40
10 4	< 1.86	- .57
10 3	5.35	- 5.67
10 2	4.39	3.63
10 1	5.56	- 6.01
10 0	11.96	-12.12
11 2	4.21	- 4.13
11 1	4.29	4.65
12 1	4.30	- 4.25

1 k l	$\lvert F_o \rvert$	F_c
0 -12	12.97	-12.05
0 -10	10.87	11.68
0 -8	7.14	7.03
0 -6	6.71	- 6.01
0 -4	23.70	-24.58
0 -2	24.00	-25.20
1 -13	5.07	- 5.19
1 -12	3.85	- 3.30
1 -11	6.96	6.74
1 -10	< 2.45	- .89
1 -9	5.01	3.61
1 -8	6.38	- 6.50
1 -7	2.87	2.07
1 -6	14.02	-13.05
1 -5	17.35	-17.98
1 -4	18.25	-18.83
1 -3	10.29	-14.41
1 -2	15.19	-14.84
1 -1	10.03	5.42
2 -13	4.25	4.03
2 -12	< 2.21	- .47
2 -11	10.54	-10.43
2 -10	8.02	6.84
2 -9	< 2.40	- 1.86
2 -8	11.71	10.41
2 -7	5.92	- 5.98
2 -6	16.48	14.57
2 -5	19.22	-17.00
2 -4	52.02	-44.41
2 -3	4.47	- 4.31
2 -2	21.69	-23.88
2 -1	8.40	- 7.70
3 -13	3.14	2.35
3 -12	3.27	- 2.45
3 -11	5.05	5.42
3 -10	4.37	2.82
3 -9	7.86	6.46
3 -8	3.82	- 5.04
3 -7	5.24	5.02
3 -6	< 1.97	.25
3 -5	11.17	- 9.02
3 -4	< 1.63	- 1.69
3 -3	10.81	-12.36
3 -2	9.30	7.98
3 -1	15.80	-14.11
4 -12	4.57	3.50
4 -11	< 2.26	.61
4 -10	< 2.43	- 2.41
4 -9	< 2.45	- .99
4 -8	< 2.40	1.45
4 -7	3.19	- 4.78
4 -6	9.59	9.23
4 -5	32.81	32.91
4 -4	21.93	-19.41
4 -3	5.01	2.27
4 -2	5.11	- 2.82
4 -1	19.75	17.66
5 -10	4.73	5.02
5 -9	< 2.45	- 1.73
5 -8	< 2.45	- 1.26
5 -7	9.03	- 8.40
5 -6	< 2.25	- .31
5 -5	< 2.12	1.20
5 -4	< 2.00	1.72
5 -3	10.75	9.54
5 -2	23.38	22.58
5 -1	5.41	4.34
6 -9	3.53	- 2.63
6 -8	4.93	- 4.47
6 -7	13.57	-13.32
6 -6	12.44	-11.08
6 -5	4.61	5.48
6 -4	18.57	19.54
6 -3	7.99	- 8.04
6 -2	5.39	6.04
6 -1	11.15	10.04
7 -11	2.31	- 1.77
7 -10	3.36	2.68
7 -9	< 2.21	- 1.25
7 -8	3.87	- 4.76
7 -7	3.46	- 2.05
7 -6	19.49	-18.70
7 -5	4.54	4.37
7 -4	16.66	-15.47
7 -3	3.88	3.59
7 -2	6.36	7.11
7 -1	4.13	4.74
8 -7	6.83	- 7.93
8 -6	5.01	- 4.05
8 -5	15.89	-14.98
8 -4	11.46	11.10
8 -3	< 2.45	1.08
8 -2	< 2.43	- 3.51
8 -1	7.71	7.87
9 -7	4.71	3.47
9 -6	5.81	- 5.49
9 -5	< 2.32	1.56
9 -4	< 2.40	- 1.83
9 -3	4.22	- 4.49

1 k l	$\lvert F_o \rvert$	F_c
9 -2	6.79	6.07
9 -1	< 2.45	- 2.55
10 -3	6.93	7.01
10 -2	< 2.26	- 1.13
10 -1	5.82	5.79
0 8	5.65	- 4.49
1 9	7.29	- 8.69
1 8	< 2.34	3.39
1 7	4.16	- 3.65
1 6	4.06	5.10
1 5	9.83	10.59
1 4	3.89	6.00
1 3	33.21	38.64
1 2	13.74	-14.42
1 1	13.21	17.67
1 0	9.31	-10.16
2 8	13.69	-14.62
2 7	< 2.21	- 1.96
2 6	9.77	- 9.77
2 5	3.40	3.09
2 4	3.25	- 3.56
2 3	29.82	31.37
2 2	24.27	25.83
2 1	51.42	-53.52
2 0	< 1.03	- 1.49
3 9	9.52	- 9.38
3 8	< 2.41	2.43
3 7	5.41	- 3.94
3 6	< 2.10	- 2.67
3 5	6.28	- 6.88
3 4	5.80	- 5.52
3 3	12.83	-13.71
3 2	6.74	- 7.15
3 1	14.29	-13.26
3 0	19.10	17.20
4 9	11.70	-11.32
4 8	7.18	- 6.37
4 7	< 2.36	- 1.31
4 6	< 2.23	- 2.21
4 5	8.11	- 8.65
4 4	3.60	- .38
4 3	7.93	6.09
4 2	14.97	-13.53
4 1	9.31	7.20
4 0	4.43	7.97
5 8	5.70	3.74
5 7	4.69	4.68
5 6	11.91	-11.28
5 5	4.21	3.28
5 4	12.17	-11.48
5 3	5.71	4.93
5 2	3.85	3.85
5 1	8.37	8.18
5 0	24.32	23.92
6 11	4.85	5.52
6 10	< 1.97	- .97
6 9	4.39	- 3.16
6 8	12.50	11.20
6 7	< 2.47	- .86
6 6	< 2.43	3.07
6 5	6.91	- 7.41
6 4	5.49	4.55
6 3	< 2.19	1.39
6 2	7.58	8.42
6 1	6.01	5.68
6 0	4.80	5.35
7 10	6.20	6.50
7 9	6.77	5.83
7 8	4.87	4.51
7 7	< 2.40	- .30
7 6	8.07	- 7.24
7 5	< 2.45	3.32
7 4	6.21	- 6.46
7 3	< 2.36	- 1.92
7 2	< 2.32	- 1.78
7 1	< 2.28	- 1.32
7 0	9.38	8.78
8 9	4.79	5.12
8 8	4.75	3.76
8 7	6.46	- 5.63
8 6	< 2.34	- 1.45
8 5	6.96	- 7.27
8 4	4.33	- 3.30
8 3	4.25	3.61
8 2	13.18	-14.65
8 1	< 2.43	- 2.90
8 0	4.02	- 3.04
9 7	3.89	- 4.13
9 6	4.08	- 3.66
9 5	< 2.25	- 1.51
9 4	8.72	- 9.05
9 3	8.33	- 8.52
9 2	< 2.43	.34
9 1	4.31	- 5.18
9 0	12.83	12.58
10 5	4.16	- 4.76
10 4	4.49	3.24
10 3	< 2.15	- 3.41
10 2	10.30	-10.52
10 1	7.23	7.46
10 0	4.15	3.38
11 4	3.30	- 3.87
11 3	3.45	3.45
11 2	< 1.80	1.57
11 1	4.22	5.11
11 0	3.89	3.46

2 k l	$\lvert F_o \rvert$	F_c
0 -12	5.40	- 4.29
0 -10	20.79	-22.68
0 -8	14.98	15.50
0 -6	9.11	9.89

2 k l	$\lvert F_o \rvert$	F_c
0 -4	9.14	-10.65
0 -2	23.85	-28.81
1 -13	5.13	- 3.65
1 -12	3.30	3.24
1 -11	7.08	- 6.88
1 -10	< 2.49	- 1.63
1 -9	5.57	5.20
1 -8	< 2.25	- 2.07
1 -7	5.39	4.51
1 -6	7.70	- 8.55
1 -5	3.43	2.84
1 -4	12.47	-14.19
1 -3	11.92	-14.22
1 -2	19.08	-21.84
1 -1	14.40	-14.24
2 -13	< 1.82	2.85
2 -12	< 2.21	- 1.34
2 -11	9.08	9.00
2 -10	< 2.49	- 1.20
2 -9	13.19	-15.38
2 -8	12.02	11.67
2 -7	< 2.10	- 1.91
2 -6	16.37	15.71
2 -5	4.95	- 5.53
2 -4	28.26	21.72
2 -3	21.46	-20.11
2 -2	45.50	-41.71
2 -1	8.24	- 7.67
3 -11	3.93	3.72
3 -10	< 2.47	- .83
3 -9	9.65	10.01
3 -8	4.02	3.44
3 -7	10.89	9.87
3 -6	4.73	- 7.04
3 -5	6.97	7.53
3 -4	2.55	- 3.23
3 -3	2.23	1.98
3 -2	4.73	.68
3 -1	11.72	-10.91
4 -11	3.30	2.72
4 -10	6.14	6.25
4 -9	< 2.49	.17
4 -8	< 2.43	- 1.71
4 -7	< 2.31	.44
4 -6	4.75	3.26
4 -5	7.63	- 7.16
4 -4	13.03	11.83
4 -3	35.65	35.75
4 -2	21.33	-19.04
4 -1	< 1.68	1.57
5 -9	3.52	- 2.17
5 -8	7.09	8.15
5 -7	4.18	- 2.80
5 -6	< 2.33	- .48
5 -5	12.44	-11.40
5 -4	6.03	- 5.89
5 -3	4.68	- 1.96
5 -2	4.90	6.44
5 -1	7.88	7.98
6 -11	4.06	5.00
6 -10	3.45	- 4.17
6 -9	3.62	3.98
6 -8	3.80	- 4.58
6 -7	< 2.49	- 1.29
6 -6	6.29	- 5.34
6 -5	13.67	-13.57
6 -4	17.00	-16.94
6 -3	3.27	5.18
6 -2	15.39	15.91
6 -1	11.60	-11.29
7 -10	3.27	2.87
7 -9	3.13	- 2.63
7 -8	5.16	4.56
7 -7	3.68	- 2.15
7 -6	3.71	- 3.80
7 -5	< 2.47	- 1.42
7 -4	21.19	-21.11
7 -3	< 2.40	- .39
7 -2	18.52	-17.01
7 -1	5.05	4.86
8 -10	4.61	4.44
8 -9	< 1.91	- .68
8 -8	< 2.14	- .75
8 -7	< 2.30	- .09
8 -6	< 2.40	2.37
8 -5	5.62	- 6.06
8 -4	3.73	- 3.34
8 -3	15.53	-16.68
8 -2	12.67	12.37
8 -1	< 2.49	- 2.91
9 -8	4.99	4.32
9 -7	< 2.02	2.08
9 -6	< 2.16	- 1.86
9 -5	5.59	5.53
9 -4	5.48	- 4.82
9 -3	3.52	2.40
9 -2	3.57	- 3.55
9 -1	3.54	- 2.52
10 -1	6.03	6.69
0 6	8.76	8.11
0 4	45.21	57.54
1 11	4.18	- 4.88
1 10	< 2.33	.74
1 9	< 2.49	- 1.53
1 8	< 2.47	2.49
1 7	5.49	6.96
1 6	< 2.16	2.39
1 5	21.34	23.05
1 4	11.81	-13.91
1 3	3.47	.95
1 2	5.14	- 5.35
1 1	2.83	- 2.23
1 0	10.41	-11.93

2 k l	$\lvert F_o \rvert$	F_c
2 10	6.38	- 6.24
2 9	< 2.47	- 1.93
2 8	3.79	- 4.27
2 7	< 2.39	2.00
2 6	< 2.23	- 2.15
2 5	12.18	11.81
2 4	12.11	12.17
2 3	28.27	-29.27
2 2	2.36	1.51
2 1	6.76	- 6.45
2 0	17.74	-18.56
3 11	5.49	- 5.75
3 10	< 2.23	1.90
3 9	< 2.43	- 1.03
3 8	< 2.49	- .02
3 7	< 2.43	- 2.67
3 6	< 2.30	- 1.37
3 5	6.92	- 7.07
3 4	8.90	- 7.66
3 3	3.60	- 5.21
3 2	12.92	12.96
3 1	10.05	-10.18
3 0	6.92	6.62
4 11	3.89	- 4.96
4 10	3.07	- 2.36
4 9	< 2.36	- .51
4 8	< 2.47	- 1.04
4 7	< 2.47	- 3.12
4 6	< 2.39	- 1.99
4 5	7.90	6.56
4 4	12.27	- 6.90
4 3	4.43	8.90
4 2	7.83	7.88
4 1	13.08	11.07
4 0	3.80	- 1.11
5 11	2.10	2.33
5 10	4.47	3.19
5 9	< 2.23	2.24
5 8	5.49	- 5.08
5 7	< 2.49	1.28
5 6	5.34	- 4.39
5 5	< 2.39	1.94
5 4	4.45	4.26
5 3	7.63	5.48
5 2	17.11	17.00
5 1	< 1.98	2.25
5 0	16.96	17.48
6 10	4.87	6.18
6 9	< 2.03	- 2.03
6 8	< 2.29	1.40
6 7	< 2.49	- 3.90
6 6	< 2.49	1.94
6 5	< 2.47	3.23
6 4	< 2.43	4.44
6 3	7.46	5.83
6 2	3.27	2.12
6 1	4.94	5.55
6 0	4.13	5.43
7 8	4.51	- 4.57
7 7	< 2.29	1.65
7 6	< 2.40	- 3.34
7 5	< 2.47	- 1.75
7 4	< 2.49	- 2.49
7 3	< 2.47	- 1.11
7 2	6.31	6.22
7 1	3.46	3.57
7 0	3.75	3.90
8 7	3.51	- 4.84
8 6	3.21	- 2.25
8 5	3.54	2.85
8 4	8.67	- 9.71
8 3	< 2.47	- 1.49
8 2	< 2.49	- 1.95
8 1	5.30	5.46
8 0	< 2.49	- 2.47
9 6	3.62	- 5.40
9 5	6.18	- 6.58
9 4	< 2.23	.44
9 3	< 2.31	- 1.51
9 2	10.65	10.22
9 1	< 2.40	- 1.83
9 0	5.36	5.32
10 4	6.60	- 6.94
10 3	6.69	6.94
10 2	3.24	2.36
10 1	3.73	4.87
10 0	< 2.18	- 1.35

still on the cold plate, placed on a small piece of dry ice and transferred to the goniometer head of the Weissenberg camera. The crystals were kept frozen by means of a cold stream of nitrogen gas.

Unit cell and space group

The crystal temperature was adjusted to -135 ± 2 °C. All diffraction data were recorded at this temperature with Cu $K\alpha$ raidation on Kodak no screen medical X-ray film. It was determined from oscillation and Weissenberg photographs that the crystals are monoclinic, space group C_{2h}^5–$P2_1/c$, the extinctions being $h0l$, l odd and $0k0$, k odd. The cell constants, determined from sodium chloride calibrated rotation and zero layer Weissenberg photographs, are

$$a=5{\cdot}55\pm0{\cdot}01,\ b=9{\cdot}664\pm0{\cdot}007,\ c=11{\cdot}341\pm0{\cdot}011\ \text{Å};$$
$$\beta=101^\circ\ 49'\pm20'$$
$$[a_0(\text{NaCl})=5{\cdot}637\ \text{Å}]\ .$$

The monoclinic angle β was determined by the method of angular lag (Buerger, 1942). The calculated density of 1·11 g.cm.$^{-3}$ with four molecules per unit cell compares well with the experimental density of 1·106 g.cm.$^{-3}$ measured at −37 °C. by Rosental (1936).

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 visually estimated employing a standard intensity strip. Correlation of the intensities of the various sets of films was made by comparison to a photograph which contained fifteen minute exposures of a twenty-five degree portion of each layer. The intensities were then corrected by the appropriate Lorentz polarization and Tunell factors. Absorption was neglected since μr was calculated to be less that 0·15. A total of 530 independent intensities were measured. Of these 126 were found to be too weak to observe.

Since both crystalline propionic and butyric acids contain hydrogen bonded dimers located about a center of symmetry, it was anticipated that crystalline valeric acid might also. It was further assumed that the molecules would be roughly planar with a perpendicular distance between adjacent valeric acid dimers of about 3·5 Å. The relatively short a axis indicates that the planes of the dimers lie close to the (100) crystallographic planes. The assumed intermolecular distance of 3·5 Å would in fact incline the plane of the dimers at an angle of approximately 40° to the (100) plane. The Patterson projection $P(vw)$ was therefore calculated and solved by the use of the above assumptions. The electron density projection $\varrho(yz)$ was then calculated using the observed scattering amplitudes with signs based on the above trial structure. All atoms were well resolved and in agreement with the proposed structure.

The structure was refined by least squares methods on an IBM 704 computer using the Vand–Sly program NYXR1. Each atom was assigned an individual isotropic temperature factor and all reflections were given unit weight. The atomic form factors used were those of McWeeny (1951) The structure factor for an unobserved reflection was taken to be one-half the minimum observable value. An initial temperature factor of 3·5 was assumed for all atoms. During the three dimensional refinement using all 530 reflections, the conventional reliability index decreased from $R=0{\cdot}37$ to $R=0{\cdot}21$ while the sum of the squares of the residuals decreased from 5,719 to 2,037. The final isotropic parameters are presented in Table 1. At this point in the refinement the various bond distances were C–O = 1·26, 1·39 Å and C–C = 1·50, 1·55, 1·57, 1·59 Å. Since the agreement was not too good, the three dimensional full matrix anisotropic Busing–Levy OR-XLS program was used. The weights for the observational equations were taken as $(F_o)^{-2}$ if $F_o \geq 4F_{\text{min.}}$ and $(4F_{\text{min.}})^{-2}$ if $F_o < 4F_{\text{min.}}$. Unobserved reflections were included as above. The atomic form factors used are those of Berghuis *et al.* (1955). The program calculated the appropriate initial anisotropic temperature factors from the final isotropic factors as input data. The initial positional parameters used were the final values obtained from the isotropic refinement. Three least squares cycles reduced the reliability index for observed reflections only to $R=0{\cdot}11$. The final calculated and observed structure factors appear in Table 2. A summary of the atomic positional parameters appears in Table 1. The general anisotropic thermal parameters have been transformed into the parameters of a Gaussian ellipsoid of vibration. The values obtained are the direction cosines of the principal axes of the ellipsoid and the root-mean-square amplitudes of vibration along those axes. These values are listed in Table 3. The root-mean-square amplitudes of vibration along the ith axis is given as $(\overline{r_i^2})^{\frac{1}{2}}$. The values T_{i1}, T_{i2}, and T_{i3} in Table 3

Table 3. *Principal-axis parameters of the atomic vibration ellipsoids*

Atom	i	$(\overline{r_i^2})^{1/2}$	T_{i_1}	T_{i_2}	T_{i_3}
O_1	1	0·188 Å	0·98957	−0·08974	−0·11246
	2	0·157	0·07199	0·98803	−0·13643
	3	0·236	0·11752	0·12924	0·98463
O_2	1	0·256	0·97125	−0·01931	−0·23722
	2	0·161	0·02481	−0·98307	0·18150
	3	0·211	0·23658	0·18266	0·95428
C_1	1	0·255	0·94315	−0·11157	−0·31309
	2	0·148	0·22812	0·90238	0·36561
	3	0·200	0·24200	−0·41600	0·87656
C_2	1	0·166	0·96237	−0·12625	0·24077
	2	0·208	0·25324	0·73822	0·62522
	3	0·211	0·09900	−0·66193	0·74302
C_3	1	0·255	0·99816	−0·05799	−0·01758
	2	0·159	0·05859	0·99771	0·03389
	3	0·206	0·01588	−0·03340	0·99930
C_4	1	0·181	0·81709	−0·47806	−0·32221
	2	0·221	0·55550	0·80447	0·21037
	3	0·236	0·16422	−0·34335	0·92474
C_5	1	0·120	0·99949	−0·02099	0·02431
	2	0·215	0·03156	0·72860	−0·68419
	3	0·237	0·00303	−0·68448	−0·72821

Table 4. *Valeric acid bond lengths and angles*

Bond	Length (Å) Isotropic temp. factors	Anisotropic temp. factors
C_5–C_4	1·58	1·57
C_4–C_3	1·57	1·57
C_3–C_2	1·55	1·53
C_2–C_1	1·50	1·53
C_1–O_1	1·39	1·35
C_1–O_2	1·26	1·26
$O_1 \cdots O_2'$	2·64	2·63

Angle	Isotropic temp. factors	Anisotropic temp. factors
C_5–C_4–C_3	111° 18′	112° 59′
C_4–C_3–C_2	107 31	109 25
C_3–C_2–C_1	111 34	113 26
C_2–C_1–O_2	127 14	124 58
C_2–C_1–O_1	115 56	116 30
O_1–C_1–O_2	116 49	118 32
C_1–$O_1 \cdots O_2'$	114 35	114 6

are the direction cosines of the ith axis with respect to the orthogonal axes parallel to a^*, b^*, and c, respectively.

Discussion of the structure

Crystalline valeric acid crystallizes as hydrogen bonded dimers located about a center of symmetry. Projections of the arrangement of the molecules in the unit cell are shown in Fig. 1. The atoms O_1, O_2, C_1 and C_2 are coplanar to within ±0·01 Å. However such planes through each member of the dimer, though parallel, are separated by 0·12 Å. The hydrogen bond is thus at an angle of 2° 34′ with respect to the planes of the acid groups. The equation of the unit normal to these planes is $N = 3{\cdot}434a^* + 0{\cdot}2824b^* + 7{\cdot}2811c^*$ where a^*, b^* and c^* are the monoclinic reciprocal lattice vectors. The carbon atoms C_3, C_4 and C_5 lie out of this plane by the perpendicular distances of −0·026, −0·159 and −0·071 Å, respectively. The final bond lengths and

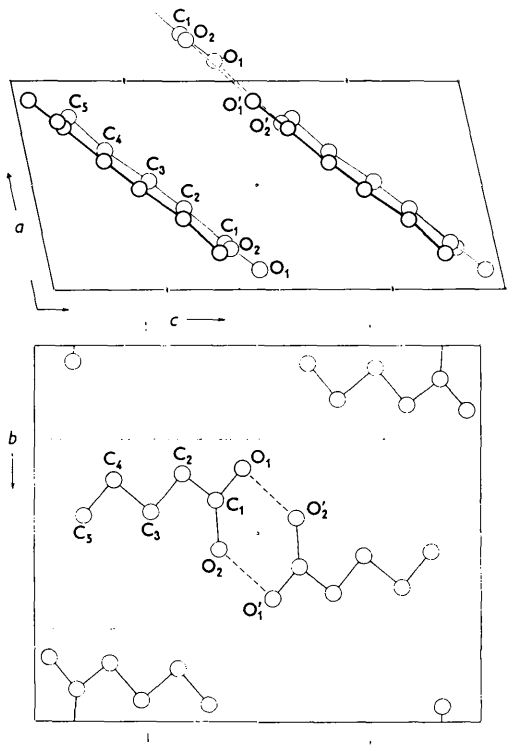

Fig. 1. Unit-cell projections of valeric acid.

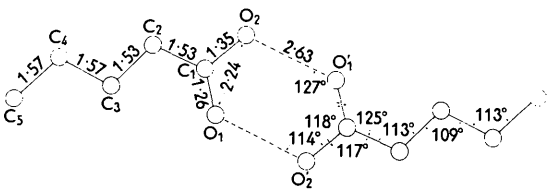

Fig. 2. Distances and angles in valeric acid.

bond angles appear in Fig. 2 and Table 4. The standard deviation of a bond distance, calculated from the least squares results is ±0·02 Å. The rather unnatural carbon–carbon distances of 1·57 Å are disturbing but are felt to be not very significantly different from the expected value of 1·54 Å. A possible explanation for this apparent bond lengthening is that the reported center of a chain carbon atom is displaced from the actual center by the presence of the neglected hydrogen atoms. Unfortunately we are unable to test this hypothesis at present due to the status of our computing facilities. All intermolecular distances are normal and comparable to those found in other acids of this series. The closest carbon–carbon and carbon–oxygen distances between adjacent molecules are 3·64 and 3·40 Å, respectively. The closest oxygen–oxygen approach, other than the hydrogen bonded distance, is 3·62 Å.

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