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The Crystal and Molecular Structure of Sodium 2-Oxovalerate

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Crystals of sodium 2-oxovalerate, $CH_3(CH_2)_2COCOONa$, grown from a water–alcohol mixture, belong to the orthorhombic space group *Pbcn* and contain eight molecules per unit cell of dimensions: $a=34{\cdot}08$, $b=6{\cdot}14$ and $c=5{\cdot}91$ Å. A least-squares refinement of the three-dimensional data, with isotropic temperature factors for all the atoms except hydrogens, brought the residual down to 12·3%. The structure consists of Na–O bonds holding the molecules into infinite layers parallel to the (100) plane. Thus molecules are tightly bound by Na–O bonds on one side and loosely by van der Waals bonds on the other.

Introduction

In sequence to a preliminary report (Jain, Tavale & Biswas, 1966) the structure analysis of sodium 2-oxovalerate, $CH_3(CH_2)_2COCOONa$, is presented in this paper.

Experimental

Sodium 2-oxovalerate, prepared by adding a concentrated solution of sodium hydroxide to the alcoholic solution of 2-oxovaleric acid, was crystallized from a water/alcohol mixture. They are orthorhombic and grow as very thin plates parallel to the (100) face. The unit-cell dimensions are: $a=34{\cdot}08$, $b=6{\cdot}08$, $c=5{\cdot}91$ Å.

These values have been obtained from high angle reflexion in the zero-layer Weissenberg photographs. The deviation of a from the mean value is $\pm 0{\cdot}025$ Å while that of b and c is $\pm 0{\cdot}030$ Å. The Weissenberg photographs were taken with single film and suitable allowances were made for the thickness of the black wrapper in deriving the unit-cell dimensions. However, other systematic errors were neglected.

The density of the crystal was measured at 25 °C by the usual flotation method to give a mean value of 1·47 g.cm^{-3} and the calculated density assuming eight molecules of $CH_3(CH_2)_2COCOONa$ per unit cell is 1·48 g.cm^{-3}.

The three-dimensional data were collected from equi-inclination Weissenberg photographs taken with Cu $K\alpha$ radiation, using the usual multiple film technique. The crystal used was roughly $0{\cdot}5\times 1{\cdot}0$ mm^2 in area. The longer side was the c axis and the zero to fourth layer was taken along this axis, while the zero layer only was taken with **b** as oscillation axis. Nearly thirty per cent of the theoretically possible reflexions were recorded. Some of the low angle reflexions were cut off by the beam stop.

The systematic absences are: $hk0$ for $h+k=$ odd, $h0l$ for l odd, $0kl$ for l odd and $h+k+l$ no condition. Hence the space group was uniquely determined as *Pbcn*. It was observed that the reflexions with $h+k+l$ even are sharp, while those with $h+k+l$ odd are diffuse, suggesting that the crystals are disordered and the type of disorder is similar to that found in sodium 2-oxocaprylate (Pant, 1964). The linear absorption coefficient μ for Cu $K\alpha$ radiation is 17·6 cm^{-1}. Intensities were measured visually and were corrected for the Lp factor in the usual way (Cochran, 1948). The intensities of higher layer spots were measured generally from extended spots and were corrected for the spot extension effect (Phillips, 1956). The intensities of some of the spots which were contracted were used without the Phillip's correction. Absorption correction was neglected.

Determination and refinement

Comparison of the unit-cell dimensions with sodium 2-oxobutyrate (Tavale, Pant & Biswas, 1963) shows that there is an increase of $\simeq 1{\cdot}5$ Å in a while b and c remain more or less equal within experimental errors. Assuming that the structure is isotypic with sodium 2-oxobutyrate this increase in a is to be expected. A trial structure, therefore, could easily be postulated.

The structure factors were calculated using McWeeny's (1951) values of atomic scattering factors for the C and O atoms; for the Na^+ ion that of James & Brindley (1931) was used.

The (001) and (010) projections were refined by the usual methods till R came down to 12·4% and 13·3% respectively. The final overall temperature factor for both these projections was 1·1 Å^2. Electron density projections along (001) and (010) are shown in Figs. 1 and 2. Three-dimensional least-squares refinement was carried out on the CDC-3600, 160-A computer installed at the Tata Institute of Fundamental Research, Bombay, incorporating simultaneous refinement of atomic parameters and individual isotropic temperature factors. The scattering factor for each asymmetric atom for each plane was calculated using analytical constants A, a, B, b and C given by Moore (1963).

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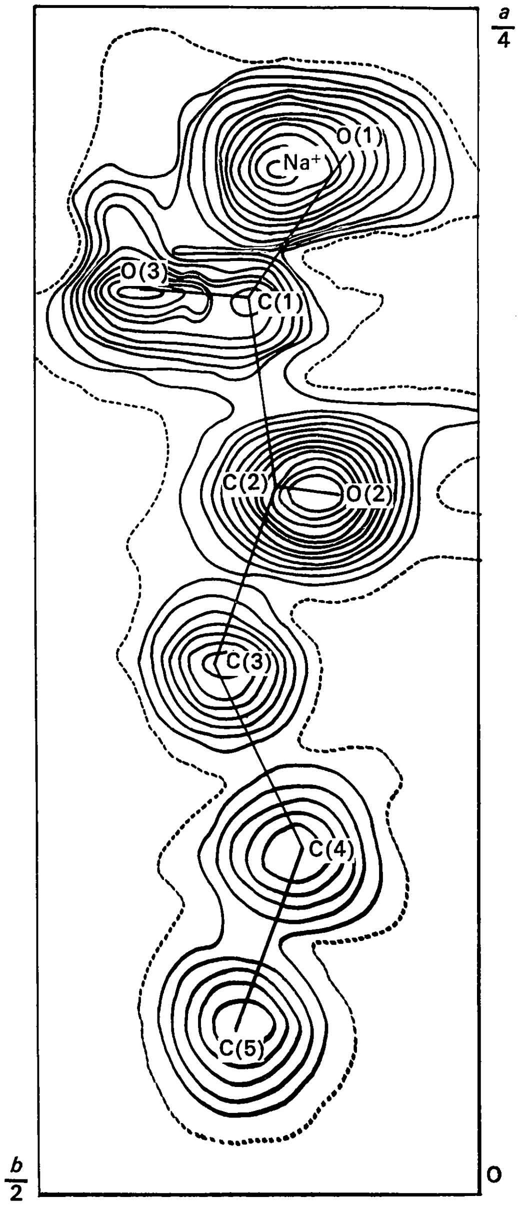

Fig. 1. Electron density projection on (001). Contours are drawn at intervals of 1 e.Å^{-2} except around Na^+ and O(1) where only the first four contours are at 1 e.Å^{-2}, the others being at intervals of 2 e.Å^{-2}; 1 e.Å^{-2} contour is dashed.

Table 2. *Observed and calculated structure factors*

h	k	l	Fo	Fc
8	0	0	81.6	-82.1
10	0	0	46.1	42.8
12	0	0	114.3	-108.3
14	0	0	107.6	106.9
16	0	0	98.9	-89.7
18	0	0	18.3	13.1
20	0	0*	5.9	9.3
22	0	0*	7.0	-4.7
24	0	0	16.3	-19.3
26	0	0	66.3	62.3
28	0	0	35.5	32.7
30	0	0	74.9	-79.6
32	0	0	35.5	48.8
34	0	0	33.6	-35.8
36	0	0	17.3	20.5
38	0	0	17.3	-15.0
40	0	0*	6.4	-1.6
42	0	0	21.1	22.5
3	1	0	10.6	-14.1
5	1	0	9.6	-8.7
7	1	0*	3.8	7.5
9	1	0	9.6	8.9
11	1	0	58.6	-56.3
13	1	0	98.9	91.6
15	1	0	25.9	-23.9
17	1	0	43.2	-25.6
19	1	0	36.5	28.0
21	1	0	38.4	-26.8
23	1	0	20.2	22.0
25	1	0	25.0	-22.7
27	1	0	18.3	16.4
2	2	0	60.5	69.3
4	2	0*	4.6	1.1
6	2	0*	4.6	4.0
8	2	0	23.1	23.9
10	2	0*	5.4	-9.7
12	2	0	57.6	60.1
14	2	0	61.5	-66.1
16	2	0	65.3	68.9
18	2	0	35.5	-27.5
20	2	0*	7.0	9.2
22	2	0*	7.5	4.2
24	2	0*	8.1	-4.8
26	2	0	37.5	-26.4
28	2	0	43.2	-33.6
30	2	0	54.7	56.1
32	2	0	23.1	-27.1
34	2	0	18.3	17.3
1	3	0	14.4	-17.9
3	3	0	32.7	42.0
5	3	0	16.3	-19.3
7	3	0*	6.0	11.9
9	3	0	10.6	-7.3
11	3	0	47.1	50.1
13	3	0	88.4	-101.7
15	3	0	12.5	11.4
17	3	0	41.3	44.1
19	3	0	25.0	-28.3
21	3	0	22.1	23.4
23	3	0	18.3	-19.7
25	3	0	27.9	28.1
27	3	0	27.9	-26.2
29	3	0*	8.6	10.1
31	3	0*	8.1	9.7
33	3	0	13.5	-15.1
35	3	0	12.5	15.3
0	4	0	32.7	29.3
2	4	0*	7.0	1.7
4	4	0*	7.0	10.7
6	4	0	16.3	-18.1
8	4	0*	7.5	-1.9
10	4	0*	7.5	3.5
12	4	0	20.2	-18.5
14	4	0	13.5	12.3
16	4	0	21.1	-20.8
18	4	0	18.3	16.2
20	4	0*	8.6	-12.7
22	4	0*	8.6	-1.2
24	4	0	16.3	17.7
26	4	0*	8.6	-5.4
28	4	0	18.3	18.7
3	5	0	26.9	-28.0
5	5	0	26.9	26.0
7	5	0	26.9	-22.5
9	5	0*	8.6	-5.3
11	5	0*	8.6	-4.7
13	5	0	31.7	28.7
15	5	0*	8.6	15.5
17	5	0	31.7	-27.6
0	6	0	22.1	-15.5
2	6	0	19.2	14.4
4	6	0*	8.6	-16.0
6	6	0*	8.6	-2.8
8	6	0	20.2	19.7
10	6	0	20.2	-18.3
12	6	0	18.3	14.2
3	1	1	53.9	58.9
4	1	1	35.6	33.0
5	1	1	23.5	20.3
6	1	1	14.0	10.7
7	1	1	34.3	-31.5
8	1	1	24.6	22.4
9	1	1	13.7	13.0
10	1	1	27.2	-35.1
11	1	1	39.2	45.2
12	1	1	72.1	62.5
13	1	1	107.6	-94.0
14	1	1	47.7	-47.8
15	1	1*	6.5	13.6
16	1	1	18.7	-13.0
17	1	1	41.1	36.4
18	1	1	37.5	31.0
19	1	1	17.7	-25.5
20	1	1	54.4	-49.9
21	1	1	16.6	14.5
22	1	1	30.0	30.5
23	1	1*	8.4	3.6
24	1	1	59.0	-55.8
25	1	1*	8.9	7.0
26	1	1	20.7	17.7
27	1	1	25.5	-28.0
28	1	1	33.7	32.9
29	1	1*	9.5	13.3
30	1	1*	7.9	-8.4
31	1	1	16.6	16.0
32	1	1	20.7	17.8
33	1	1*	9.5	-16.2
34	1	1	20.2	-20.7
1	2	1	25.3	-21.1
2	2	1	49.0	58.0
3	2	1	18.7	-18.4
4	2	1	13.7	11.8
5	2	1	36.5	37.4
6	2	1	34.3	-32.7
7	2	1	30.0	-25.9
8	2	1	27.5	26.8
9	2	1*	4.9	-4.3
10	2	1*	6.0	-1.4
11	2	1	27.5	-20.4
12	2	1*	6.5	8.9
13	2	1*	5.4	-6.5
14	2	1	37.3	-34.9
15	2	1	46.9	37.5
16	2	1	17.9	19.6
17	2	1	15.0	-15.9
18	2	1	18.6	15.7
19	2	1	25.3	25.3
20	2	1	17.7	-19.1
21	2	1	23.4	-23.3
22	2	1*	8.4	2.1
23	2	1*	7.4	2.0
24	2	1	19.6	20.4
25	2	1	18.7	16.0
26	2	1	27.5	-27.8
27	2	1	19.7	-16.7
1	3	1	18.6	17.3
2	3	1	20.7	-20.3
3	3	1	27.5	-28.6
4	3	1	46.9	-54.8
5	3	1*	6.5	11.6
6	3	1	47.7	53.5
7	3	1*	6.5	-5.8
8	3	1	58.1	-67.3
9	3	1	11.7	-13.1
10	3	1	42.2	46.3
11	3	1	18.6	21.4
12	3	1	28.1	-28.7
13	3	1*	7.8	-5.6
14	3	1	15.0	13.6
15	3	1	17.7	18.1
16	3	1	15.0	11.0
17	3	1	18.6	-10.5
18	3	1	18.7	-17.0
19	3	1*	8.9	-10.1
20	3	1	36.5	37.5
21	3	1*	8.9	14.3
22	3	1	33.7	-33.5
23	3	1	16.6	-19.9
24	3	1	45.0	47.0
25	3	1*	9.5	11.6
26	3	1	21.5	-21.1
27	3	1*	9.5	6.0
28	3	1	18.2	-10.7
29	3	1*	9.5	-10.2
30	3	1*	7.9	-4.8
31	3	1*	8.9	4.0
32	3	1*	7.4	-3.3
33	3	1*	8.4	-3.7
34	3	1*	6.8	11.7
35	3	1*	7.8	0.3
36	3	1	15.9	-15.9
37	3	1*	6.5	2.5
38	3	1	16.9	15.1
0	4	1	28.4	36.1
1	4	1*	6.3	10.3
2	4	1*	7.8	-6.6
3	4	1*	6.3	7.0
4	4	1	13.7	-13.3
5	4	1	11.2	-9.0
6	4	1*	8.4	4.0
7	4	1*	6.8	-1.8
8	4	1*	8.4	4.2
9	4	1	14.0	16.1
10	4	1	18.6	-19.6
11	4	1	15.9	21.5
12	4	1*	8.9	7.7
13	4	1*	7.4	-5.1
14	4	1	23.5	24.9
15	4	1	19.7	-18.2
16	4	1	22.6	-24.3
17	4	1	15.0	-13.7
4	5	1	18.7	23.5
5	5	1*	9.5	2.8
6	5	1	36.5	-36.7
7	5	1*	9.5	1.7
8	5	1	49.7	54.3
9	5	1*	9.5	6.6
10	5	1	32.8	-38.9
11	5	1	19.6	-19.3
12	5	1	20.7	20.2
13	5	1	16.6	16.8
14	5	1*	7.9	-9.6
15	5	1*	9.5	-8.7
16	5	1*	7.9	0.5
17	5	1*	9.5	-5.0
18	5	1*	7.9	7.4
19	5	1*	9.5	11.3
20	5	1	34.7	-31.6
21	5	1*	9.5	-8.0
22	5	1	43.1	37.0
23	5	1*	8.9	8.2
24	5	1	43.1	-34.3
0	6	1	19.6	7.0
1	6	1	15.0	-12.7
2	6	1*	9.5	-14.7
3	6	1*	7.9	9.4
4	6	1*	9.5	7.8
5	6	1*	7.9	-10.9
6	6	1*	9.5	6.4
7	6	1*	7.9	9.8
8	6	1*	9.5	-6.2
9	6	1*	7.9	-6.2
10	6	1*	8.9	12.0
11	6	1	23.4	-24.5
12	6	1*	8.9	-10.6
13	6	1	15.9	13.1
14	6	1*	8.9	-3.1
15	6	1*	7.4	2.8
16	6	1*	8.4	5.5
17	6	1	20.7	22.9
18	6	1*	8.4	-1.2
19	6	1	26.9	-19.3
0	0	2	115.7	124.3
1	0	2*	6.0	15.1
2	0	2	39.6	-41.5
3	0	2*	6.0	-2.4
4	0	2	61.2	59.4
5	0	2	53.8	46.5
6	0	2	59.3	-57.0
7	0	2	55.7	-55.9
8	0	2	12.2	-15.0
9	0	2	10.6	-9.0
10	0	2	70.6	64.8
11	0	2	17.3	-16.9
12	0	2	96.9	-91.4
13	0	2	13.5	-19.5
14	0	2	12.2	13.8
15	0	2	74.9	60.2
16	0	2	35.7	-29.2
17	0	2	31.7	-30.8
18	0	2	56.5	53.1
19	0	2	55.7	50.9
20	0	2	47.3	-44.9
21	0	2	31.7	-30.7
22	0	2	14.1	8.9
23	0	2	13.5	-10.9
24	0	2	27.3	26.3
25	0	2*	10.2	14.6
26	0	2*	10.2	-8.1
27	0	2	18.3	-17.5
28	0	2	32.7	30.7
29	0	2	25.0	24.1
30	0	2	30.1	-32.6
31	0	2*	9.4	-11.1
32	0	2	18.8	19.0
33	0	2*	8.6	2.3
34	0	2	27.3	-28.2
35	0	2*	8.4	-9.4
36	0	2	20.4	17.3
38	0	2	15.1	-5.3
40	0	2	19.8	-20.6
1	1	2	19.6	-11.2
2	1	2	28.4	22.5
3	1	2*	4.7	-0.3
4	1	2	31.1	-29.5
5	1	2	28.9	24.9
6	1	2	47.6	55.6
7	1	2	36.3	-33.3
8	1	2	44.9	-45.1
9	1	2	15.9	12.3
10	1	2*	6.2	4.8
11	1	2	15.4	8.9
12	1	2	20.2	15.3
13	1	2*	6.1	-3.9
14	1	2	16.5	-17.0
15	1	2	13.1	8.4
16	1	2	15.6	7.9
0	2	2	99.1	-112.1
1	2	2	28.4	-33.3
2	2	2	50.3	49.3
3	2	2*	6.2	-0.8
4	2	2	42.8	-40.7
5	2	2*	6.9	-0.7
6	2	2	18.6	23.7
7	2	2*	6.9	5.0
8	2	2	21.4	24.1
9	2	2	20.2	22.4
10	2	2	53.1	-51.6
11	2	2*	7.5	9.8
12	2	2	66.2	70.2
13	2	2*	7.5	6.4
14	2	2	18.6	-15.7
15	2	2	24.8	-25.6
16	2	2	26.1	20.5
17	2	2*	8.7	-7.7
18	2	2	30.7	-28.6
19	2	2*	8.7	-3.9
20	2	2	21.4	22.2
21	2	2*	9.4	3.3
22	2	2*	8.7	-5.2
23	2	2*	10.0	3.4
24	2	2	17.7	-13.0
25	2	2*	10.0	9.8
26	2	2*	8.8	-2.6
27	2	2	23.3	-20.7
29	2	2*	10.0	-9.4
30	2	2	27.0	27.8
31	2	2*	9.4	7.6
32	2	2	20.5	-19.2
33	2	2*	9.4	-2.4
34	2	2	27.0	20.7
35	2	2*	8.2	7.8
36	2	2	14.0	-15.1
1	3	2	15.9	19.2
2	3	2	19.2	-17.6
3	3	2*	6.6	-6.2
4	3	2	25.0	11.8
5	3	2	26.1	-27.7
6	3	2	47.6	-48.5
7	3	2	39.1	41.8
8	3	2	44.9	47.2
9	3	2	20.5	-17.3
10	3	2*	8.2	-9.0
11	3	2*	7.7	-4.9
13	3	2*	7.7	-9.5
14	3	2*	8.7	-4.7
15	3	2*	8.3	-7.2
16	3	2*	9.4	-5.9
17	3	2*	8.3	4.1
18	3	2*	9.2	-7.0
19	3	2*	9.2	5.0
20	3	2*	10.0	0.2
21	3	2*	8.8	8.7
22	3	2	20.2	20.1
23	3	2	21.4	-20.2
24	3	2*	10.0	-8.5
25	3	2	21.4	16.6
0	4	2	58.7	71.4
1	4	2*	9.4	22.6
2	4	2	39.1	-39.2
3	4	2*	9.4	12.7
4	4	2*	8.3	16.7
5	4	2	32.9	-33.5
6	4	2*	8.3	5.3
7	4	2	27.5	22.6
8	4	2	23.3	-21.5
9	4	2*	9.4	-9.4
10	4	2	25.2	23.5
11	4	2*	10.0	-14.3
12	4	2	22.7	-34.3
13	4	2*	10.4	7.2
14	4	2	19.6	16.8
15	4	2*	10.0	-1.5
16	4	2	17.7	-13.7
17	4	2	33.9	27.2
18	4	2*	8.8	3.7
19	4	2	28.4	-31.4
20	4	2*	8.8	1.9
21	4	2	24.8	21.6
22	4	2*	8.8	1.6
23	4	2*	10.0	1.5
24	4	2*	8.3	-1.4
25	4	2	22.9	-24.2
26	4	2*	8.3	8.4
27	4	2	20.2	20.9
28	4	2*	7.7	9.2
29	4	2*	8.2	-3.0
30	4	2	22.4	-18.4
31	4	2*	6.9	-2.0
32	4	2	20.5	16.3
33	4	2*	6.2	-3.2
34	4	2	15.9	-14.3
1	5	2*	9.9	-12.9
2	5	2*	10.0	3.0
3	5	2*	8.8	6.3
4	5	2	19.2	20.4
5	5	2*	8.8	9.4
6	5	2*	10.0	-7.9
7	5	2	17.7	-15.2
8	5	2*	10.0	0.8
9	5	2*	8.8	5.8
10	5	2*	10.0	-1.3
11	5	2*	8.8	-5.1
12	5	2	19.6	-16.4

Table 1. *Final atomic parameters*

	x	y	z	B (Å^2)
Na	0·2166 ± 0·0002	0·2366 ± 0·0008	−0·0010 ± 0·0008	1·62
O(1)	0·2193 ± 0·0002	0·1516 ± 0·0011	0·3962 ± 0·0011	1·24
O(2)	0·1507 ± 0·0002	0·1601 ± 0·0011	0·1774 ± 0·0011	2·03
O(3)	0·1931 ± 0·0002	0·3837 ± 0·0011	0·6599 ± 0·0011	1·57
C(1)	0·1915 ± 0·0003	0·2576 ± 0·0014	0·4866 ± 0·0014	1·60
C(2)	0·1513 ± 0·0003	0·2272 ± 0·0014	0·3649 ± 0·0014	2·01
C(3)	0·1157 ± 0·0003	0·3000 ± 0·0014	0·5014 ± 0·0014	1·53
C(4)	0·0782 ± 0·0003	0·2062 ± 0·0014	0·3936 ± 0·0014	2·30
C(5)	0·0410 ± 0·0003	0·2770 ± 0·0014	0·5341 ± 0·0014	4·08

Table 2 (*cont.*)

h	k	l	Fo	Fc
13	5	2	20.5	23.0
14	5	2	22.0	16.2
15	5	2*	8.8	- 0.4
17	5	2*	8.3	- 8.9
18	5	2*	9.6	- 1.8
19	5	2*	8.3	3.0
20	5	2*	9.4	4.7
21	5	2*	8.3	- 9.5
22	5	2*	8.7	- 14.3
23	5	2	19.6	16.8
24	5	2*	8.2	0.9
25	5	2	18.6	- 15.1
0	6	2	24.2	- 27.5
1	6	2*	9.4	4.0
2	6	2	21.4	19.8
3	6	2*	9.4	- 12.2
4	6	2	22.0	19.4
6	6	2*	8.3	- 5.0
7	6	2*	9.6	- 6.2
8	6	2	13.1	10.1
9	6	2	15.6	- 12.9
10	6	2	12.5	- 5.0
11	6	2	19.2	16.2
12	6	2	14.0	11.7
1	1	3	16.3	- 12.6
2	1	3*	5.9	2.2
3	1	3	24.0	23.7
4	1	3	57.1	49.8
5	1	3*	6.8	- 5.5
6	1	3	79.5	- 71.1
7	1	3	19.2	30.0
8	1	3	88.8	76.0
9	1	3	16.3	- 18.0
10	1	3	27.1	- 24.0
11	1	3*	8.1	2.9
12	1	3	36.5	36.5
13	1	3	23.1	- 34.9
14	1	3	20.6	- 22.6
15	1	3*	8.7	- 5.0
16	1	3	24.4	- 29.5
17	1	3*	10.0	8.4
18	1	3	17.8	16.8
19	1	3*	10.0	1.6
20	1	3	29.0	- 28.2
21	1	3	17.3	17.4
22	1	3	38.3	38.0
23	1	3*	10.9	- 7.8
24	1	3	39.3	- 40.9
25	1	3*	10.9	7.7
26	1	3	21.5	20.9
27	1	3	18.3	- 15.8
0	2	3	36.5	- 38.9
1	2	3	19.7	13.2
2	2	3	21.1	19.5
3	2	3*	7.0	- 5.7
4	2	3	18.3	- 18.5
5	2	3	38.3	- 35.0
6	2	3	16.3	15.9
7	2	3	36.5	35.0
8	2	3	14.4	10.4
9	2	3*	8.2	- 6.9
10	2	3	15.4	- 13.3
11	2	3	18.7	- 15.0
12	2	3	15.4	13.0
13	2	3*	8.7	7.7
14	2	3	22.1	- 18.3
15	2	3*	9.3	- 3.7
16	2	3	17.3	14.9
17	2	3	23.4	26.5
18	2	3*	9.6	- 9.0
19	2	3	30.0	- 38.0
20	2	3*	10.9	15.0
21	2	3	21.5	20.5
22	2	3*	10.9	- 7.2
23	2	3	19.2	13.6
24	2	3*	10.9	- 1.9
25	2	3	21.5	- 18.9
2	3	3*	8.7	- 2.9
3	3	3	21.1	- 12.6
4	3	3*	8.7	- 8.2
5	3	3*	9.3	- 5.7

h	k	l	Fo	Fc
6	3	3*	8.7	3.1
7	3	3*	10.0	2.9
8	3	3	19.7	- 20.0
9	3	3*	10.0	- 10.3
10	3	3	28.0	27.6
11	3	3*	10.0	15.3
12	3	3	56.1	- 59.7
13	3	3*	10.0	7.7
14	3	3	43.0	45.7
15	3	3*	10.9	10.7
16	3	3*	10.2	12.3
17	3	3*	10.9	- 6.7
18	3	3	25.3	- 27.6
19	3	3*	10.9	- 8.0
20	3	3	28.0	37.9
21	3	3*	10.9	5.4
22	3	3	28.0	- 34.2
23	3	3*	10.9	- 13.5
24	3	3	25.3	31.2
25	3	3*	10.2	7.9
26	3	3	19.7	- 18.1
27	3	3*	10.3	3.2
28	3	3*	9.3	- 2.9
29	3	3*	10.0	- 5.1
30	3	3*	8.7	12.5
31	3	3*	8.7	- 1.7
32	3	3	21.5	- 20.8
33	3	3*	8.1	- 0.9
34	3	3	19.7	16.7
0	4	3	21.1	21.6
1	4	3	20.6	24.4
2	4	3*	10.9	- 1.9
3	4	3*	10.3	- 1.6
4	4	3*	10.9	4.8
5	4	3	15.4	14.4
6	4	3*	10.9	- 12.2
7	4	3*	10.2	- 7.3
8	4	3*	10.9	- 4.9
9	4	3*	10.2	- 12.9
10	4	3*	10.9	- 1.1
11	4	3	25.3	25.8
1	5	3*	10.9	- 1.3
2	5	3*	10.2	- 12.0
4	5	3*	10.9	9.3
5	5	3*	10.9	9.3
6	5	3*	10.2	8.0
7	5	3	20.2	- 15.8
8	5	3*	10.2	0.2
9	5	3	20.2	16.1
10	5	3	18.7	- 17.3
11	5	3*	10.9	- 13.2
12	5	3	35.5	35.4
13	5	3*	10.9	2.5
14	5	3	29.0	- 25.1
15	5	3*	10.2	- 6.5
16	5	3*	9.6	- 7.6
17	5	3*	10.0	3.1
18	5	3	23.4	22.2
19	5	3*	10.0	5.4
20	5	3	28.0	- 24.2
21	5	3*	9.3	- 11.4
22	5	3	18.7	12.0
23	5	3	18.3	16.6
0	6	3*	10.0	- 2.7
1	6	3	27.1	- 30.0
1	0	4	48.0	49.5
2	0	4*	8.8	- 8.3
3	0	4*	9.4	- 16.4
4	0	4	24.5	20.7
5	0	4	14.4	- 19.0
6	0	4	16.9	- 14.0
7	0	4*	9.7	10.9
8	0	4*	8.6	10.4
9	0	4	14.4	- 20.0
10	0	4	28.2	26.8
11	0	4*	10.0	- 0.5
12	0	4	44.3	- 46.7
13	0	4	13.5	- 11.8
14	0	4	15.1	- 16.6
15	0	4	24.0	22.2
16	0	4*	10.1	0.9

h	k	l	Fo	Fc
17	0	4*	10.8	10.2
18	0	4	31.0	31.3
19	0	4*	10.8	- 8.5
20	0	4	16.0	- 13.2
25	0	4	19.2	- 19.9
1	1	4	10.6	- 7.7
2	1	4	10.5	7.1
3	1	4*	5.1	0.4
4	1	4*	6.0	3.3
5	1	4	14.4	10.3
6	1	4*	6.4	- 8.0
7	1	4*	5.6	- 1.4
8	1	4*	6.4	6.0
9	1	4*	6.0	- 8.3
10	1	4*	7.0	9.5
11	1	4	15.4	15.8
12	1	4	18.3	- 22.8
13	1	4	14.4	- 15.1
14	1	4	14.9	17.5
15	1	4	12.5	9.7
16	1	4*	7.5	- 0.7
17	1	4*	7.4	- 0.5
18	1	4	14.9	- 10.3
19	1	4*	7.6	- 7.3
20	1	4*	8.8	8.9
21	1	4	14.4	13.0
0	2	4	34.6	- 38.2
2	2	4	31.7	32.4
3	2	4*	7.0	3.8
4	2	4	29.8	- 27.8
5	2	4*	7.5	6.3
6	2	4	13.5	6.6
7	2	4*	7.5	4.0
8	2	4	15.6	7.4
9	2	4*	8.0	8.1
10	2	4	35.5	- 37.6
11	2	4*	8.1	5.0
12	2	4	39.4	49.7
13	2	4*	8.6	2.4
14	2	4*	7.4	4.9
15	2	4*	8.6	- 12.2
16	2	4*	7.4	0.6
17	2	4*	8.8	- 5.0
18	2	4	17.3	- 21.5
19	2	4*	8.8	- 2.7
20	2	4	13.5	9.4
1	3	4	15.4	19.4
2	3	4	16.6	- 16.5
3	3	4	10.6	- 9.7
4	3	4*	8.6	1.9
5	3	4	14.4	- 12.2
6	3	4*	8.6	2.9
7	3	4*	7.7	0.7
8	3	4*	8.6	- 6.0
9	3	4*	7.4	7.7
10	3	4*	8.6	- 8.8
11	3	4	16.3	- 13.2
12	3	4	23.6	24.3
13	3	4	13.5	12.3
14	3	4	17.5	- 17.2
15	3	4*	7.6	- 7.1
16	3	4*	8.8	- 3.0
17	3	4*	8.6	0.7
18	3	4*	8.8	13.5
19	3	4*	7.6	5.0
20	3	4*	8.8	- 7.1
21	3	4*	7.6	- 12.4
22	3	4*	8.8	5.6
23	3	4*	7.4	1.8
24	3	4*	8.6	- 2.0
25	3	4*	8.9	3.6
26	3	4*	8.1	8.5
27	3	4	20.9	17.1
28	3	4*	7.0	- 11.3
29	3	4	15.4	- 9.1
0	4	4	36.5	51.2

* indicates unobserved reflexion.
020 appeared to suffer from extinction and therefore was not included in the refinement.

Table 2 (*cont.*)

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
1	4	4	8.8	- 19.6	2	5	4	8.6	9.0	9	6	4	6.4	10.4
2	4	4	34.6	- 43.4	3	5	4	16.3	11.2	10	6	4	15.4	- 12.2
3	4	4	8.8	4.2	4	5	4	8.6	- 2.8	11	6	4	6.9	- 6.9
4	4	4	26.9	29.7	5	5	4	6.7	9.3	12	6	4	15.4	15.3
5	4	4	6.8	5.7	6	5	4	8.6	7.2	0	0	6	33.6	50.2
6	4	4	7.6	- 2.9	7	5	4	7.4	- 4.1	1	0	6	10.8	- 13.6
7	4	4	8.8	- 10.3	8	5	4	8.6	- 0.8	2	0	6	35.7	- 30.3
8	4	4	19.2	- 17.3	9	5	4	7.4	6.1	3	0	6	10.8	- 9.6
9	4	4	8.8	- 4.1	10	5	4	6.9	- 3.4	4	0	6	10.1	- 6.1
10	4	4	33.6	33.9	11	5	4	11.5	- 9.2	5	0	6	10.5	- 3.0
11	4	4	8.8	- 1.6	12	5	4	9.1	2.6	6	0	6	24.8	19.5
12	4	4	36.5	- 39.2	13	5	4	11.5	9.9	7	0	6	10.5	3.1
13	4	4	8.8	7.3	0	6	4	20.2	- 22.5	8	0	6	11.3	- 6.5
14	4	4	16.3	12.6	1	6	4	6.4	6.9	9	0	6	10.6	- 13.8
15	4	4	11.5	- 6.5	2	6	4	20.2	20.9	10	0	6	9.4	13.4
16	4	4	13.5	- 9.6	3	6	4	6.4	1.9	11	0	6	14.4	13.0
17	4	4	13.5	6.1	4	6	4	18.3	- 18.6	12	0	6	25.5	- 23.6
18	4	4	14.4	13.0	5	6	4	6.4	- 3.5	13	0	6	9.7	8.6
19	4	4	8.6	8.2	6	6	4	5.6	5.6	14	0	6	9.1	3.5
20	4	4	13.5	- 8.3	7	6	4	6.4	- 0.5	15	0	6	24.0	- 23.6
21	5	4	16.3	- 18.2	8	6	4	11.5	8.3	16	0	6	8.8	- 0.6
										17	0	6	15.4	17.6

The disorder is explained as for the case of sodium 2-oxocaprylate (Pant, 1964), where it has been shown that the structure is close to the ordered structure of space group *Pbcn*, except that the intensities of reflexions with indices $h+k+l$ odd are reduced, owing to the diffuseness caused by some disorder. If, therefore, the intensities of diffuse spots are measured at their reciprocal lattice points and scaled separately, they would behave as if they were sharp reflexions. Their inclusion in the three-dimensional refinement was expected to give more reliable results. The *R*-index was 16·54% at the start, after the necessary separate scaling of all the reflexions, sharp as well as diffuse. Scale factors were calculated for each layer as $K = \Sigma |F_c| / \Sigma |F_o|$, excluding very intense reflexions. This type of scaling was done repeatedly during the process of refinement. Thus the structure was refined to $R \simeq 12{\cdot}3\%$. The refinement was again carried out including all the unobserved reflexions, taking their intensity $\mu \simeq I_{min}/3$. The *R* value at the start was 18·80%, which then remained steady at 18·43%. The final parameters together with their standard deviations are listed in Table 1 and the observed and calculated structure factors in Table 2.

Discussion of the structure

Illustrations of the structure viewed along [001] and [010] are shown in Figs. 3 and 4 respectively. It will be seen that there are six short bonds between Na(x,y,z) and the neighbouring oxygen atoms. These distances together with the intermolecular distances are shown in the Figures. The packing of molecules is essentially similar to that in sodium 2-oxobutyrate.

The bond lengths and bond angles found in the 2-oxovalerate group are shown in Fig. 5 and listed in Table 3, together with their standard deviations.

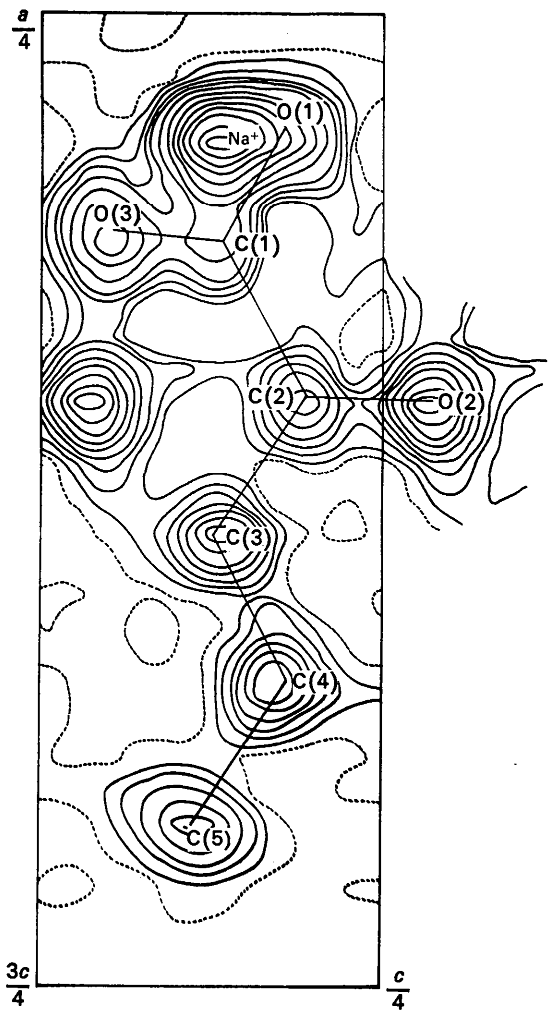

Fig. 2. Electron density projection on (010). Contours are drawn at intefvals of 1 e.Å^{-2} except around Na$^+$, O(1) and O(3) where only the first five contours are at 1 e.Å^{-2}, the others being at 2 e.Å^{-2}; 1 e.Å^{-2} contour is dashed.

Table 3. *Bond lengths and angles*

Bond lengths		Bond angles	
C(1)–O(1)	1·268 ± 0·011 Å	O(1)–C(1)–O(3)	127·7 ± 0·8°
C(1)–O(3)	1·285 ± 0·011	O(1)–C(2)–C(2)	113·7 ± 0·8
C(1)–C(2)	1·559 ± 0·012	O(3)–C(1)–C(2)	118·5 ± 0·8
C(2)–O(2)	1·182 ± 0·011	C(1)–C(2)–C(3)	114·9 ± 0·7
C(2)–C(3)	1·523 ± 0·012	C(1)–C(2)–O(2)	119·3 ± 0·8
C(3)–C(4)	1·540 ± 0·012	C(3)–C(2)–O(2)	125·8 ± 0·8
C(4)–C(5)	1·578 ± 0·012	C(3)–C(3)–C(4)	109·4 ± 0·7
		C(3)–C(4)–C(5)	110·3 ± 0·7

The mean planes through different atoms have been calculated, referred to the axes of the unit cell. The equations of these planes are as follows:

(1) $-0{\cdot}2032X-0{\cdot}7773Y+0{\cdot}5948Z+0{\cdot}8483=0$,

(2) $0{\cdot}0809X+0{\cdot}9273Y-0{\cdot}3655Z-0{\cdot}9332=0$,

(3) $0{\cdot}0811X-0{\cdot}8161Y+0{\cdot}5737Z-0{\cdot}5286=0$.

X, Y and Z are expressed in Å units.

The deviations of the atoms from their mean plane are set out in Table 4. The angles between planes 1 and 2, 1 and 3 and 2 and 3 are 17·2°, 16·5° and 16·5° respectively.

Table 4. *Deviations of atoms from their mean plane*

	Plane 1	Plane 2	Plane 3
O(1)	−0·002	—	—
O(2)	—	+0·011	—
O(3)	−0·002	—	—
C(1)	+0·002	+0·011	—
C(2)	−0·002	−0·011	−0·010
C(3)	—	+0·011	−0·010
C(4)	—	—	−0·010
C(5)	—		+0·010

The average bond length C–C is 1·550 Å, which does not differ significantly from the standard value of 1·545 Å. The bond C(4)–C(5) is rather unusually long (Fig. 5, 1·578 Å). A similar, unnatural bond (1·57 ± 0·02 Å) has been recently reported in the structure of valeric acid (Scheuerman & Sass, 1962). The minor bond length variation may be attributed partially to

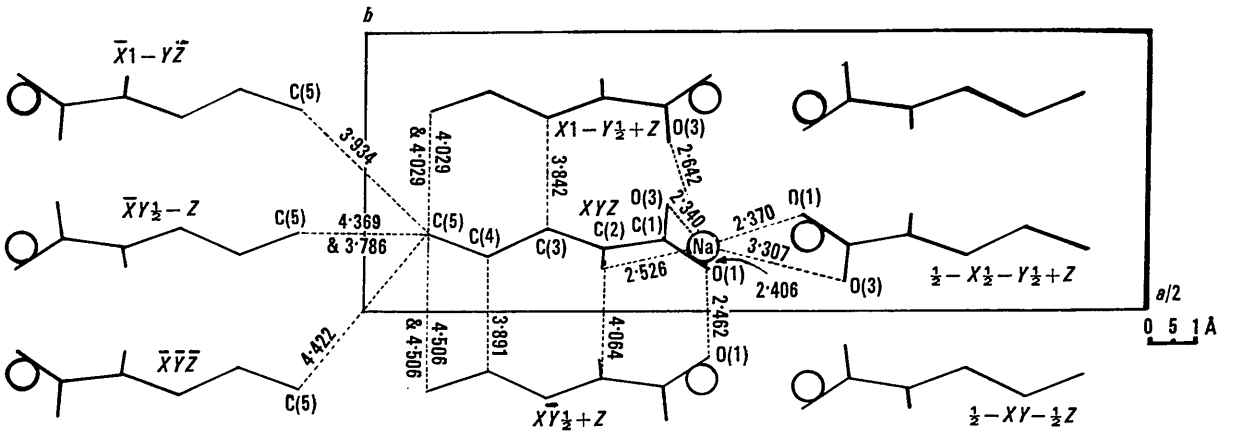

Fig. 3. The structure projected on (001).

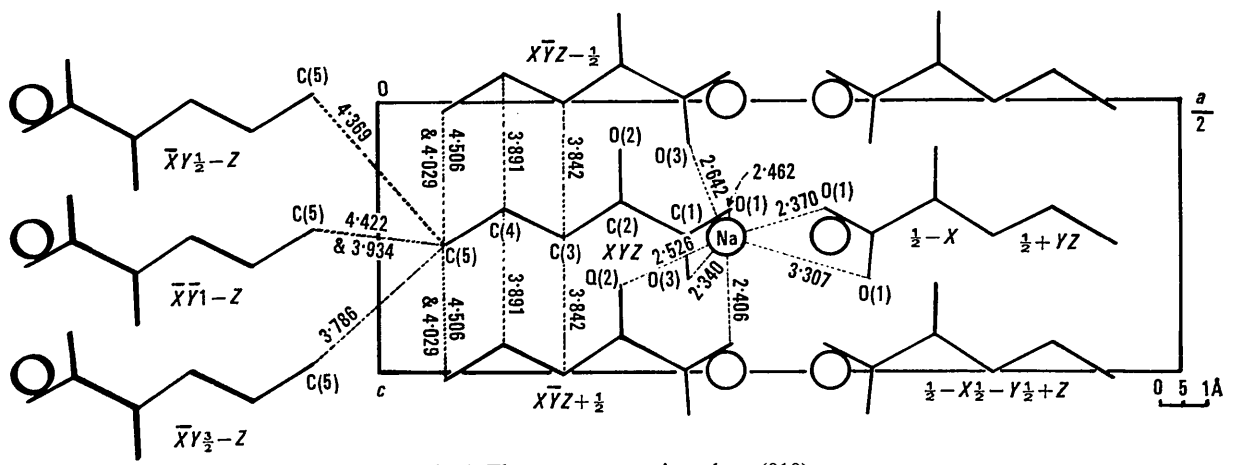

Fig. 4. The structure projected on (010).

the presence of neglected hydrogen atoms. The hydrogen atoms' contributions make up nearly 10% of the total electrons of the molecule. The inclusion of hydrogen atoms normally has a marked effect on the parameters of the carbon atoms, and tends to improve C–C distances as has been demonstrated for sebacic acid, pimelic acid and dodecanedioic acid (Housty & Hospital, 1966*a*, *b*, *c*. The quality of the data, however, did not encourage us to attempt the location of hydrogen atoms.

The carboxylate group is planar. The predicted configuration of the carboxylate ion (Pauling, 1960) has an angle O–C–O = 125·27° and equal distances C–O = 1·27 Å. Our results O(1)–C(1)–O(3) = 127·7°, C(1)–O(1) = 1·268 ± 0·011 Å and C(1)–O(3) = 1·285 ± 0·011 Å are suggestive of an almost purely ionic form of the carboxylate group in the present compound. Many examples are available in the literature of the carboxylate groups being found to have the two C–O distances equal, but varying from 1·25 to 1·29 Å. Besides an ionic carboxylate group, certain other factors could result in the equal C–O distances, *e.g.* the environments of the two oxygen atoms being identical, as in monopyridinecopper(II) acetate (orthorhombic form) (Hanic, Štempelová & Hanicová, 1964) where the C–O distances are 1·248 ± 0·020, 1·236 ± 0·019, 1·250 ± 0·022 and 1·250 ± 0·023 Å; or the structure existing in the zwitterionic form as in β-alanine, where the C–O distances are 1·292 and 1·287 ± 0·009 Å (Jose & Pant, 1964).

The crystal structure analysis of sodium 2-oxoheptylate, $CH_3(CH_2)_3COCOONa$, has been completed and a paper is in preparation.

We are grateful to Dr L. M. Pant for some helpful discussions.

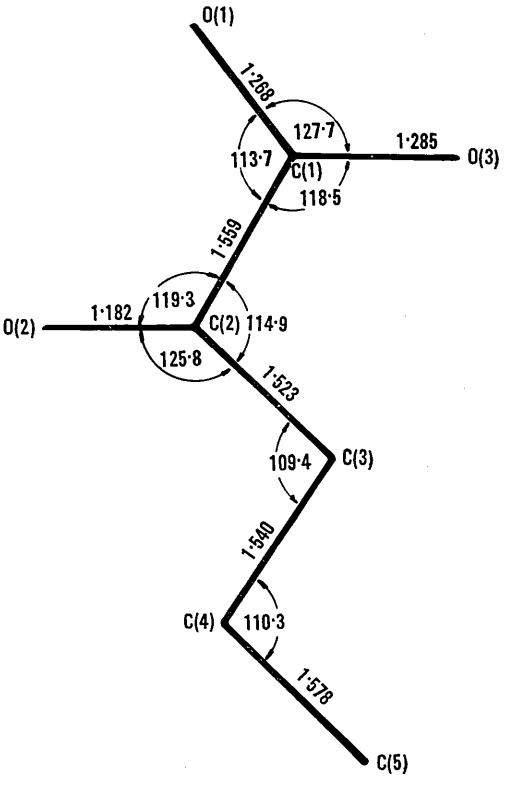

Fig. 5. Bond lengths (Å) and bond angles (°) in the 2-oxovalerate group.

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