The Crystal and Molecular Structure of Sodium 2-Oxocaprylate

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Sodium 2-oxocaprylate, $CH_3(CH_2)_5COCOONa$, is orthorhombic, space group *Pbcn*, with eight molecules per unit cell of dimensions

$$a = 49.57, \quad b = 6.05, \quad c = 5.97 \text{ Å} .$$

The structure is isotypic with that of sodium 2-oxobutyrate. Unlike sodium 2-oxobutyrate, however, enolization does not seem to occur in this compound.

Introduction

In continuation of our work on the structures of the sodium salts of α-oxo acids (Tavale, Pant & Biswas, 1961, 1963), we report in the present paper the structure analysis of sodium 2-oxocaprylate,

$$CH_3(CH_2)_5COCOONa .$$
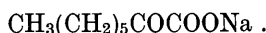
Experimental

Crystals were grown from an aqueous solution containing a trace of acetic acid. They are orthorhombic and grow as fine needles, elongated along the *c* axis. The unit cell has

$$a = 49.57, \quad b = 6.05, \quad c = 5.97 \text{ Å} .$$

a was determined separately from seven axial reflexions in the zero layer Weissenberg photograph; the standard deviation of the mean value is 0.026 Å. *b* was determined from 020 as well as 040 reflexions, both values being 6.05 Å. *c* was determined from the mean value of ζ_1, the 001 spacing of the reciprocal cell, obtained from the first and second layer line spacings on the rotation photograph along *c*; the difference between the values of *c*, obtained from the two layers separately is 0.035 Å.

The observed density at 28.5 °C, measured by the flotation method is 1.317 g.cm^{-3}, and the calculated density for eight molecules of $CH_3(CH_2)_5COCOONa$ per unit cell is 1.336 g.cm^{-3}.

From the systematic absences, the space group is uniquely determined as *Pbcn*. The linear absorption coefficient μ for Cu $K\alpha$ radiation is 13.5 cm^{-1}. The specimen used was obtained with difficulty and is a flake of roughly (0.3×4.2) mm^2 area, the longer side being the oscillation axis. The intensity data were obtained with Cu $K\alpha$ radiation by the multiple film technique from zero, first, second, third and fourth layer equi-inclination Weissenberg photographs along the

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c axis. The reflexions with $h+k+l$ even are sharp and those with $h+k+l$ odd are diffuse, thereby suggesting that the crystal is disordered; the disorder is fully described in the following paper by one of us (Pant, 1964). The structure analysis was carried out with the help of sharp reflexions only. Of the 215 possible reflexions of the type $hk0$, 73 were observed, while 56, 84, 22 and 40 sharp reflexions of the types $hk1$, $hk2$, $hk3$ and $hk4$ respectively were observed out of possible 176, 204, 155 and 161 respectively. The low angle reflexions 200, 400, 600, 800, 110 and 310 could not be recorded as they were cut off by the beam stop. Intensities were measured visually and corrected for Lp factor in the usual way (Cochran, 1948). The intensities of higher layer spots were generally measured from the extended ones and were corrected for the effect of spot extension by the method of Phillips (1956). No correction was applied for some reflexions for which only contracted spots were available. Absorption was neglected.

Structure factors were calculated with McWeeny's (1951) values of atomic scattering factors for carbon and oxygen and James & Brindley's (1931) values for Na$^+$.

Determination and refinement of the structure

The unit cell dimensions of sodium 2-oxocaprylate and sodium 2-oxobutyrate (Tavale, Pant & Biswas, 1963) are similar except that *a* in the oxocaprylate is greater by about 20 Å. Assuming usual bond lengths and angles, this is the expected increase in *a* for a structure isotypic with sodium 2-oxobutyrate, because in the latter there are four molecules in a cell, arranged in sequence nearly parallel to the *a* axis; an increase of about 5 Å in the length of each molecule (the expected increase from oxobutyrate to oxocaprylate) will thus mean an increase of 20 Å in *a*. A trial structure could therefore be easily postulated for the (001) projection. This was refined by the usual methods till *R*, on inclusion of all except high angle unobserved reflexions at half the minimum observable value, was
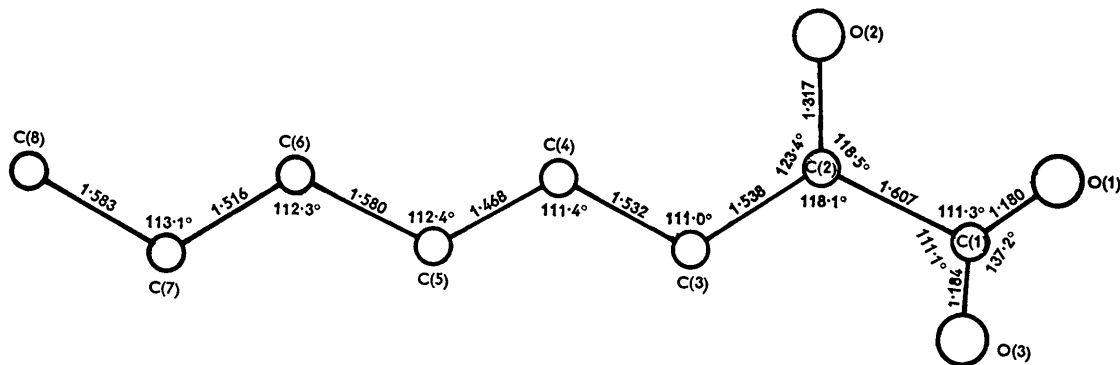
Fig. 1. Bond lengths and bond angles in the 2-oxocaprylate group. O(1) and O(3) are carboxylic oxygen atoms; O(2) is ketonic oxygen; C(3), C(4), C(5), C(6), and C(7) are methylene carbon atoms, and C(8) is the methyl carbon atom.

0·128. Isotropic temperature factors were obtained at one stage for each atom, but did not seem to improve the agreement index, so an average value of 3·6 $\mathring{A}^2$ was used for all atoms.

A trial structure was similarly postulated for the (010) projection. This structure refined to $R \sim 0\cdot2$ but there were serious discrepancies between F_o and F_c for some reflexions which could not be removed. The trial was therefore suitably modified, and this refined to $R \sim 0\cdot16$ with $B = 3\cdot6$ $\mathring{A}^2$. At this stage, some of the bond lengths appeared unlikely, so the trial structure was altered again. This structure was repeatedly refined till R, on including unobserved reflexions was 0·119. Some of the bond lengths, specially C(1)–O(1) (1·14 Å), C(1)–O(3) (1·17 Å) and C(2)–O(2) (1·40 Å) still appeared unlikely (Fig. 1). Since there were only 41 observed reflexions of the type $h0l$, and the x parameters were already well refined from the $hk0$ reflexions, it was felt that the z parameters were still not accurate in spite of the low value of R. Further refinement of z parameters was therefore done with the help of hkl reflexions. At first R, with inclusion of unobserved reflexions, was 0·275, which came down to 0·262 (0·237 for observed reflexions only) after two cycles of least-squares refinement. In obtaining R, $hk0$ reflexions were excluded; 022 shows serious disagreement between F_o and F_c and was also excluded. The 022 reflexion appears at the edge of the range of oscillation in the photograph and its estimated intensity is likely to be uncertain. Part of the disagreement between F_o and F_c is, however, due to the neglect of the hydrogen atoms whose contribution to F_c, obtained by approximately fixing their positions with the help of difference maps and from stereochemical considerations is 25. The final atomic parameters are listed in Table 1, and F_o and F_c (observed reflexions only) in Table 2.

The standard deviations of atomic coordinates and interatomic distances were estimated (Lipson & Cochran, 1953) assuming $p = 5$ $\mathring{A}^{-2}$, and $\sigma(F) \sim 0\cdot13$ $|F|$ for $hk0$ and 0·24 $|F|$ for hkl; the deviations in bond angles were estimated by the method of Darlow (1960). The estimated deviations in intramolecular bond

Table 1. *Final atomic parameters*

	x/a	y/b	z/c
Na	0·2274	0·2315	0·029
O(1)	0·2285	0·1579	0·427
O(2)	0·1817	0·1589	0·202
O(3)	0·2109	0·3773	0·682
C(1)	0·2118	0·2557	0·527
C(2)	0·1828	0·2334	0·409
C(3)	0·1577	0·2992	0·545
C(4)	0·1319	0·2132	0·434
C(5)	0·1077	0·2992	0·546
C(6)	0·0808	0·2109	0·436
C(7)	0·0559	0·2849	0·563
C(8)	0·0287	0·2343	0·434

lengths are 0·025 Å, 0·023 Å and 0·017 Å in C–C, C–O and Na–O bond lengths respectively, and the estimated average deviations in bond angles are 1·5°, 1·6° and 1·9° in C–C–C, C–C–O and O–C–O angles respectively. These estimates do not take account of the fact that the z parameters have been refined using reflexions with $h + k + l$ even only. For crystals of space group $Pbcn$, the neglect of reflexions with $h + k + l$ odd amounts to weighting the structure by half and superposing it on its reflexion on (001); and although the right structure from the two possible positions of each atom could be deduced from bond length considerations, the accuracy of z parameters was reduced, specially for atoms near $z = 0\cdot5$, because the structure factor formulae for $h + k + l$ even involve a term $\cos 2\pi lz$, which changes very slowly near $z = 0\cdot5$.

Description of the structure and discussion

Molecular structure

The bond lengths and angles found in the 2-oxocaprylate group are shown in Fig. 1 and listed in Table 3. The mean plane through the atoms O(3), O(1), C(1), C(2) can be represented by the equation

$$0\cdot187x + 0\cdot791y - 0\cdot583z - 1\cdot381 = 0 ,$$

where x, y, z are expressed in Å and referred to the axes of the unit cell. The normal distances of the

Table 2. *Observed and calculated structure factors*

h k l	|Fo|	Fc	h k l	|Fo|	Fc	h k l	|Fo|	Fc	h k l	|Fo|	Fc
10 0 0	43	41	7 5 0	23	-22	20 0 2	54	-48	14 4 2	14	12
12 0 0	81	-82	9 5 0	23	23	22 0 2	39	25	16 4 2	16	-16
14 0 0	42	41	19 5 0	32	-40	24 0 2	45	-49	18 4 2	13	11
16 0 0	85	-85	23 5 0	23	25	26 0 2	54	51	20 4 2	13	-20
18 0 0	92	88	2 1 1	165	193	28 0 2	49	-52	26 4 2	14	-9
20 0 0	121	-131	4 1 1	30	25	30 0 2	41	32	28 4 2	15	9
22 0 0	78	84	6 1 1	23	32	32 0 2	14	-7	2 1 3	29	39
24 0 0	73	-72	8 1 1	27	16	34 0 2	17	-13	4 1 3	16	16
26 0 0	22	15	10 1 1	14	10	36 0 2	35	38	6 1 3	24	-26
30 0 0	25	-22	12 1 1	30	17	40 0 2	19	19	8 1 3	43	46
38 0 0	74	72	14 1 1	25	-26	42 0 2	36	-34	10 1 3	47	-46
42 0 0	61	-57	16 1 1	39	40	44 0 2	13	12	12 1 3	49	44
44 0 0	31	36	18 1 1	68	-40	46 0 2	14	-13	14 1 3	27	-24
46 0 0	34	-38	20 1 1	63	36	48 0 2	13	10	16 1 3	16	7
48 0 0	23	21	22 1 1	19	-25	50 0 2	16	-15	18 1 3	26	-3
50 0 0	20	-20	24 1 1	26	-11	52 0 2	12	10	20 1 3	25	3
5 1 0	15	15	26 1 1	27	5	54 0 2	11	-6	1 2 3	29	29
7 1 0	9	1	28 1 1	37	-30	1 1 2	6	-5	3 2 3	16	-23
11 1 0	12	12	30 1 1	26	16	3 1 2	9	3	5 2 3	17	1
13 1 0	17	20	32 1 1	36	-40	5 1 2	15	17	7 2 3	17	21
15 1 0	34	-35	34 1 1	20	17	7 1 2	35	-33	9 2 3	17	-27
17 1 0	44	56	36 1 1	41	-46	9 1 2	47	47	11 2 3	18	20
19 1 0	107	-99	38 1 1	21	29	11 1 2	42	-41	13 2 3	17	-9
21 1 0	36	37	40 1 1	41	42	13 1 2	30	27	21 2 3	21	-13
23 1 0	20	11	1 2 1	48	-16	15 1 2	8	4	13 3 3	24	22
27 1 0	34	29	3 2 1	23	-9	17 1 2	24	-19	15 3 3	29	-29
29 1 0	25	-25	5 2 1	25	23	19 1 2	14	0	17 3 3	35	33
31 1 0	22	22	7 2 1	27	-28	21 1 2	15	-12	19 3 3	30	-26
33 1 0	20	-18	9 2 1	26	22	23 1 2	17	10	2 0 4	23	-26
35 1 0	19	17	11 2 1	14	-9	25 1 2	12	5	4 0 4	9	13
37 1 0	19	-18	17 2 1	31	32	27 1,2	12	-7	6 0 4	11	-12
0 2 0	291	-325	21 2 1	55	-50	29 1 2	12	2	8 0 4	11	8
2 2 0	79	78	23 2 1	15	10	0 2 2	65	-153	10 0 4	10	2
4 2 0	25	-25	25 2 1	16	-11	2 2 2	35	44	12 0 4	6	-6
6 2 0	25	27	27 2 1	18	19	4 2 2	27	-27	14 0 4	11	10
8 2 0	20	18	29 2 1	17	-17	6 2 2	28	45	16 0 4	22	-21
12 2 0	25	28	31 2 1	18	13	8 2 2	16	-20	18 0 4	20	24
16 2 0	39	40	2 3 1	35	-60	12 2 2	22	28	20 0 4	16	-9
18 2 0	46	-43	4 3 1	14	-30	14 2 2	33	-34	22 0 4	10	5
20 2 0	78	78	6 3 1	25	15	16 2 2	45	50	24 0 4	8	-10
22 2 0	57	-54	8 3 1	35	-51	18 2 2	36	-38	26 0 4	10	9
24 2 0	50	55	10 3 1	39	39	20 2 2	28	36	28 0 4	11	-3
26 2 0	26	-24	12 3 1	41	-47	22 2 2	22	-17	1 1 4	4	0
28 2 0	17	12	14 3 1	37	38	24 2 2	21	24	5 1 4	5	5
34 2 0	19	-4	16 3 1	33	-30	26 2 2	21	-18	7 1 4	5	-4
36 2 0	19	-16	18 3 1	16	15	28 2 2	19	19	9 1 4	5	-1
38 2 0	31	-40	28 3 1	27	22	30 2 2	13	-10	11 1 4	5	2
42 2 0	36	41	30 3 1	28	-15	42 2 2	21	24	15 1 4	7	2
44 2 0	23	-21	32 3 1	35	35	44 2 2	14	-9	17 1 4	12	1
46 2 0	23	22	34 3 1	35	-22	46 2 2	14	11	19 1 4	13	-3
3 3 0	29	27	36 3 1	36	35	48 2 2	14	-8	0 2 4	20	-26
5 3 0	34	-38	17 4 1	23	-31	1 3 2	12	7	2 2 4	13	23
7 3 0	22	23	21 4 1	23	35	3 3 2	12	-8	4 2 4	13	-14
13 3 0	20	-24	6 5 1	19	-5	5 3 2	10	-12	6 2 4	12	14
15 3 0	31	28	8 5 1	21	27	7 3 2	25	31	8 2 4	6	-9
17 3 0	49	-47	10 5 1	30	-26	9 3 2	35	-50	12 2 4	7	8
19 3 0	96	108	12 5 1	34	32	11 3 2	35	46	14 2 4	16	-15
21 3 0	35	-29	14 5 1	24	-25	13 3 2	24	-35	16 2 4	21	21
23 3 0	28	-28	16 5 1	24	20	19 3 2	13	18	18 2 4	16	-21
25 3 0	23	21	18 5 1	19	-8	23 3 2	13	-15	20 2 4	8	7
27 3 0	31	-32	2 0 2	26	-24	31 3 2	15	-13	1 3 4	8	3
29 3 0	22	23	4 0 2	27	25	33 3 2	15	16	3 3 4	7	2
31 3 0	19	-19	6 0 2	68	-86	35 3 2	17	-14	17 3 4	12	-4
35 3 0	20	-18	8 0 2	46	64	0 4 2	45	73	19 3 4	13	5
37 3 0	20	22	10 0 2	42	-48	2 4 2	29	-30	21 3 4	8	-1
39 3 0	20	-20	12 0 2	22	-21	4 4 2	16	19	14 4 4	11	15
0 4 0	43	43	14 0 2	44	43	8 4 2	16	-13	16 4 4	16	-15
24 4 0	31	-17	16 0 2	76	-73	10 4 2	17	11	18 4 4	13	13
5 5 0	23	24	18 0 2	56	57	12 4 2	15	-19			
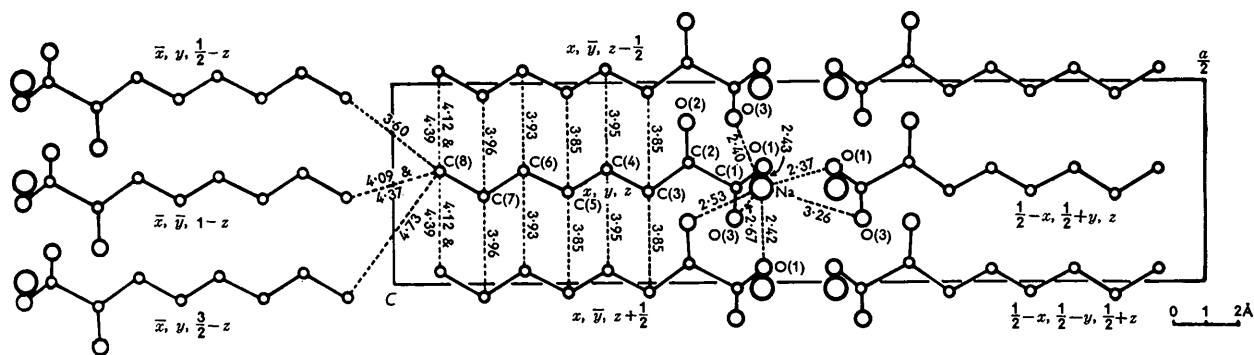
Fig. 2. Structure projected on (010).

Table 3. *Intramolecular bond lengths and angles*

	Bond lengths		Bond angles
C(1)–O(1)	1·180 Å	O(1)–C(1)–O(3)	137·2°
C(1)–O(3)	1·184	O(1)–C(1)–C(2)	111·3
C(1)–C(2)	1·607	O(3)–C(1)–C(2)	111·1
C(2)–O(2)	1·317	C(1)–C(2)–C(3)	118·1
C(2)–C(3)	1·538	C(1)–C(2)–O(2)	118·5
C(3)–C(4)	1·532	C(3)–C(2)–O(2)	123·4
C(4)–C(5)	1·468	C(2)–C(3)–C(4)	111·0
C(5)–C(6)	1·580	C(3)–C(4)–C(5)	111·4
C(6)–C(7)	1·516	C(4)–C(5)–C(6)	112·4
C(7)–C(8)	1·583	C(5)–C(6)–C(7)	112·3
		C(6)–C(7)–C(8)	113·1

individual atoms from the mean plane are 0·009 Å for O(1), O(3) and C(2) and −0·025 Å for C(1).

Referred to the same axes, the mean plane through the atoms C(1), C(2), O(2) and C(3) can be represented by the equation

$$0·078x + 0·936y - 0·343z - 1·190 = 0 .$$

The normal distances of the indvidual atoms from the mean plane are −0·001 Å for C(1), O(2) and C(3) and 0·002 Å for C(2).

The two planes make an angle of 17·3° with each other; the corresponding angle for sodium pyruvate is 18·1° (Tavale, Pant & Biwas, 1961).

The least-squares plane through the atoms C(2), C(3), C(4), C(5), C(6) and C(7), obtained by the method of Schomaker, Waser, Marsh & Bergman (1959) can be represented by the equation

$$0·033x - 0·835y + 0·549z - 0·502 = 0 .$$

The normal distances of the individual atoms from this plane are −0·039 Å for C(2), 0·031 Å for C(3), 0·061 Å for C(4), −0·046 Å for C(5), −0·005 Å for C(6), −0·004 Å for C(7) and −0·216 Å for the methyl carbon C(8). The angle between this plane and the one passing through C(1), C(2), O(2) and C(3) is 14·7°.

Unlike sodium 2-oxobutyrate (Tavale, Pant & Biswas, 1963), enolization does not seem to occur in sodium 2-oxocaprylate. This is clear from the length of the C(2)–C(3) bond (1·538 Å) which is close to the

single C–C bond length (1·545 Å), and the angle C(2)–C(3)–C(4) (111·0°) which is close to the tetrahedral angle; the corresponding values for sodium 2-oxobutyrate are 1·376 Å and 118·6° respectively. It is seen that the atoms C(1), C(2), O(2) and C(3) are coplanar within experimental error in the cases of sodium pyruvate and sodium 2-oxocaprylate, while in sodium 2-oxobutyrate, the atom O(2) is 0·426 Å away from the plane containing atoms C(1), C(2) and C(3). It seems reasonable to conclude that this distortion from planarity in sodium 2-oxobutyrate is caused by the enolization of the molecule.

The C(2)–O(2) bond length (1·317 Å) is larger than that expected in the pure keto form (1·183 Å in sodium pyruvate). It may be that this increase is related to the shortening of the C–O bonds of the caboxylic group (1·180 Å and 1·184 Å).

As in sodium pyruvate and sodium 2-oxobutyrate, the observed C(1)–C(2) bond length (1·607 Å) is longer than the standard single C–C bond length.

Crystal structure

The projection of the structure along the *b* axis is shown in Fig. 2. The intermolecular distances are also given in the figure. The structure is isotypic with that of sodium 2-oxobutyrate.

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