tural studies are being continued on the even members of the series, *i.e.* Al_6C_3N and $Al_8C_3N_4$, where the arrangement of the blocks is more symmetrical.

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The Crystal and Molecular Structure of Sodium α-Ketobutyrate*

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Sodium α-ketobutyrate, $CH_3CH_2COCOONa$, crystallized from aqueous solution, is orthorhombic, space group *Pbcn*, with eight molecules per unit cell of dimensions

$$a = 29{\cdot}28,\ b = 6{\cdot}045,\ c = 5{\cdot}90\ \text{Å}\ .$$

The detailed structure has been determined by two-dimensional Fourier, difference Fourier and least-squares methods.

The observed bond lengths and angles show that sodium α-ketobutyrate is enolized to a great extent in the crystalline state.

The crystal structures of sodium α-ketobutyrate and sodium pyruvate are similar. In both, the Na–O bonds tie the molecules into infinite double layers; any double layer is linked with the neighbouring double layers by van der Waals bonds.

Introduction

In a recent paper, the structure analysis of sodium pyruvate was reported (Tavale, Pant & Biswas, 1961). It was felt that a comparison of its crystal and molecular structure with those of its higher homologues should be of interest. Consequently, we started X-ray studies of the crystal structures of sodium α-ketobutyrate, $CH_3CH_2COCOONa$ and sodium α-ketocaprylate, $CH_3(CH_2)_5COCOONa$. The investigation of the structure of sodium α-ketocaprylate is still in progress. In the present paper, we report the structure analysis of sodium α-ketobutyrate.

Experimental details

Crystals were obtained from aqueous solution. They are orthorhombic and grow as very thin plates parallel to the (100) face. There is strong cleavage parallel to the plates. The unit cell has

$$a = 29{\cdot}28,\ b = 6{\cdot}045,\ c = 5{\cdot}90\ \text{Å}\ ,$$

these values being obtained from zero-layer Weissenberg photographs.

The observed density at 24 °C, measured by the flotation method, is $1{\cdot}562\ \text{g.cm}^{-3}$ and the calculated density for eight molecules of $CH_3CH_2COCOONa$ per unit cell is $1{\cdot}578\ \text{g.cm}^{-3}$.

The systematic absences are: $0kl$ for k odd, $h0l$ for l odd and $hk0$ for $h+k$ odd, so that the space group is uniquely determined as *Pbcn*. The linear absorption coefficient μ for Cu $K\alpha$ radiation is $19{\cdot}6\ \text{cm}^{-1}$. Reflexions of the type $hk0$ and $h0l$ were obtained from zero-layer Weissenberg photographs, using Cu $K\alpha$ radiation and the multiple-film technique. Of the 127 possible $hk0$ reflexions and 112 possible $h0l$ reflexions, 92 and 76 respectively were observed. The specimens used were flakes of roughly $(0{\cdot}5 \times 0{\cdot}7)\ \text{mm}^2$ area,

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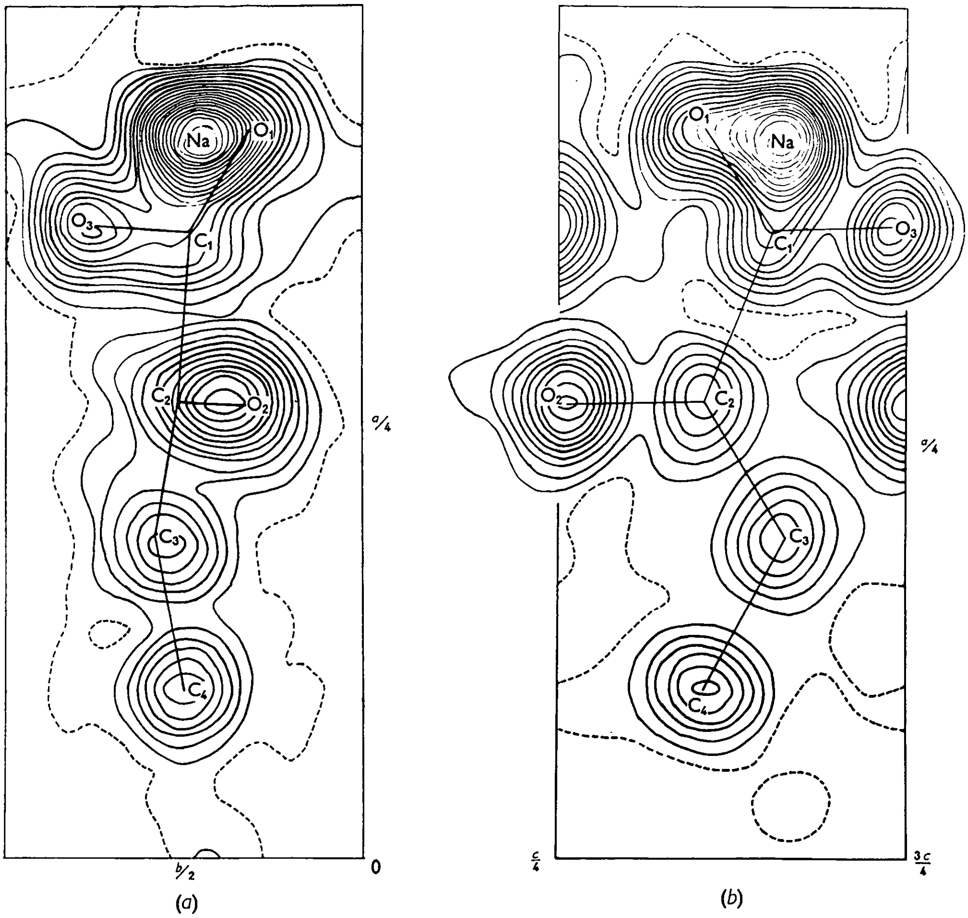

Fig. 1. (*a*) Electron density projected on (001). (*b*) On (010). Contours drawn at intervals of 1 e.Å^{-2}. 1 e.Å^{-2} contour is dashed.

the longer side being the oscillation axis. Intensities were measured visually and corrected for Lorentz and polarization factor in the usual way. No absorption correction was applied.

Wilson's method (1942) was used to obtain preliminary values for the scale factors and the temperature factors. These values were improved during the later stages of refinement. Final structure factors were calculated using McWeeny's (1951) values of atomic scattering factors for carbon and oxygen and James & Brindley's values for Na$^+$.

Determination and refinement of the structure

The approximate coordinates of the sodium atom were determined from the (001) and (010) Patterson projections, obtained with the help of the von Eller photosommateur. From the unit-cell dimensions and the expected length of the molecules, it became clear that the molecules must be arranged nearly parallel to the a axis in sequence. On plotting the sodium atoms in the (001) projection, it seemed likely that as in the structure of sodium pyruvate (Tavale, Pant & Biswas, 1961), the Na–O bonds tie the molecules into infinite layers parallel to the (100) planes. A trial structure could thus be postulated, and this gave some agreement between the observed and calculated structure factors $F(hk0)$. The x parameters could be improved by plotting $\varrho(x00)$ line synthesis, using observed $F(h00)$ and calculated signs. The x and y parameters were then refined by the usual methods till R was about 0·195.

Using the known x parameters and assuming the

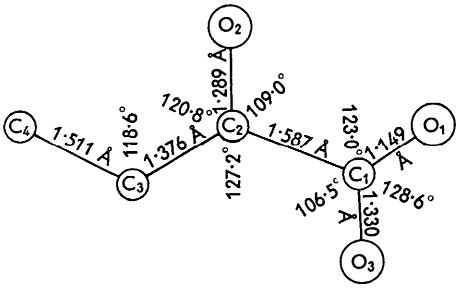

Fig. 2. Bond lengths and bond angles in the α-ketobutyrate group; O_1 and O_3 are carboxylic oxygens, O_2 is keto group oxygen, C_3 and C_4 are methylene and methyl carbons respectively.

Table 1. *Final atomic and thermal parameters*

	x/a	y/b	z/c	$B(hk0)$	$B(h0l)$
Na	0·2111 ± 0·0005	0·2450 ± 0·0025	0·0762 ± 0·0025	2·0 Å^2	1·8 Å^2
O_1	0·2136 ± 0·0007	0·1578 ± 0·0033	0·4599 ± 0·0034	2·4	2·3
O_2	0·1330 ± 0·0007	0·1642 ± 0·0033	0·2584 ± 0·0034	2·9	2·8
O_3	0·1855 ± 0·0007	0·3769 ± 0·0033	0·7312 ± 0·0034	2·2	2·4
C_1	0·1838 ± 0·0009	0·2381 ± 0·0045	0·5566 ± 0·0046	1·6	1·4
C_2	0·1336 ± 0·0009	0·2542 ± 0·0045	0·4564 ± 0·0046	3·4	3·2
C_3	0·0938 ± 0·0009	0·2865 ± 0·0045	0·5758 ± 0·0046	2·5	2·9
C_4	0·0488 ± 0·0009	0·2481 ± 0·0045	0·4568 ± 0·0046	2·4	2·7

Table 2. *Observed and calculated structure factors*

hkl	$\lvert F_o\rvert$	F_c
200	53	−157
400	39	−45
600	39	39
800	89	−77
10,0,0	94	87
12,0,0	145	−143
14,0,0	59	58
*16,0,0	21	3
18,0,0	12	−17
20,0,0	—	−2
22,0,0	53	46
24,0,0	26	25
26,0,0	58	−58
28,0,0	29	27
30,0,0	22	−25
110	5	5
310	6	−6
510	6	−9
710	7	7
910	32	43
11,1,0	53	−66
13,1,0	16	21
15,1,0	22	20
17,1,0	17	−19
19,1,0	17	17
21,1,0	18	−22
23,1,0	16	16
25,1,0	< 6	0
27,1,0	8	−10
29,1,0	8	10
020	123	−230
220	48	65
420	12	13
620	< 3	4
820	29	31
10,2,0	37	−41
12,2,0	69	85
14,2,0	51	−46
16,2,0	23	19
18,2,0	6	0
20,2,0	6	−9
22,2,0	23	−22
24,2,0	25	−25
26,2,0	37	43
28,2,0	17	−15
30,2,0	15	14
130	16	−13
330	26	28
530	14	−13
730	< 4	−3
930	39	−37
11,3,0	58	62
13,3,0	13	−10
15,3,0	32	−29
17,3,0	18	15
19,3,0	14	−12
21,3,0	21	24
23,3,0	22	−19
25,3,0	8	4
27,3,0	5	6
29,3,0	12	−11
040	25	36
240	< 6	0
440	12	11
640	14	−17
840	14	−12
10,4,0	10	6
12,4,0	24	−25
14,4,0	21	20
16,4,0	20	−19
18,4,0	8	9
20,4,0	16	15
22,4,0	< 6	1
24,4,0	22	15
26,4,0	21	−19
150	9	5
350	24	−22
550	24	27
750	< 6	−4
950	< 6	−5
11,5,0	14	−2
13,5,0	8	−12
15,5,0	17	13
060	26	−23
260	17	7
460	9	−9
660	14	−3
860	23	20
10,6,0	9	−7
12,6,0	9	8
14,6,0	< 6	4
16,6,0	7	−1
002	62	82
102	54	−52
202	21	−24
302	27	33
402	60	61
502	< 6	−1
602	49	−52
702	12	−11
802	38	−35
902	65	72
10,0,2	37	33
11,0,2	38	−32
12,0,2	50	−49
13,0,2	18	−18
14 0 2	44	44
15 0,2	18	−17
16,0,2	60	−62
17,0 2	14	6
18 0,2	37	37
19,0,2	< 9	6
20,0,2	17	20
21,0,2	< 9	−5
22,0,2	16	−13
23,0,2	11	4
24,0,2	26	29
25,0,2	< 10	−7
26,0,2	26	−27
27,0,2	11	15
28,0,2	11	14
29,0,2	< 10	−10
30,0,2	17	−17
004	50	49
104	< 9	−20
204	14	−14
304	15	15
404	20	−22
504	10	2
604	21	24
704	< 9	4
804	< 9	−1
904	30	32
10,0,4	10	−10
11,0,4	21	−18
12,0,4	20	−17
13,0,4	9	−9
14,0,4	< 10	−3
15,0,4	20	−19
16,0,4	22	28
17,0,4	14	4
18,0,4	10	−13
19,0,4	< 10	3
20,0,4	11	−10
21,0,4	< 10	−5
22,0,4	25	22
006	50	−45
106	< 10	−1
206	27	23
306	< 10	9
406	12	2
506	< 10	8
606	12	−4
706	12	−10
806	< 10	11
906	23	20
10,0,6	21	−19
11,0,6	10	0
12,0,6	15	16
13,0,6	23	−22
14,0,6	9	−9
15,0,6	9	9

* Reflexion 16,0,0 seems to be overlapping with a spurious reflexion.

usual bond lengths and angles, a reasonable trial structure could be postulated for the (010) projection. This structure was refined as usual till R was about 0·19. The bond lengths and the angle C_2–C_3–C_4 (Fig. 2) in the α-ketobutyrate group, obtained at this stage suggested an appreciable degree of enolization of the compound. Further, the C_1–C_2 bond length (Fig. 2) came out to be unusually long (1·588 Å). In order to confirm that these observations are significant, the structure was further refined. Before the final refinement of atomic parameters, the individual temperature factors for both projections were obtained for each atom by the least-squares method. In the later least-squares refinements of atomic parameters, the off-diagonal terms were included where necessary, to account for the overlapping of atoms, and uncertain structure factors were suitably weighted. The difference Fourier maps failed to reveal the hydrogen-atom positions with certainty. The final value of R, on including all except very-high-angle unobserved reflexions at half the minimum observable value, was 0·159 for $hk0$ and 0·140 for $h0l$ reflexions. In obtaining R, reflexions 200 and 020 were excluded as they appear to be subject to extinction and 20,0,0 was omitted because it coincides with the 22,0,0 reflexion of Cu $K\beta$ radiation in the photographs, and hence its observed value is uncertain. Some reflexions with $h > 30$ were observed, but these were left out from the calculations.

The (001) and (010) electron-density projections, shown in Fig. 1, were obtained using final calculated signs and F_o values for all except $F(200)$ and $F(020)$ for which final F_c values were used. The final atomic and thermal parameters are listed in Table 1, and the observed and calculated structure factors in Table 2.

The standard deviations of atomic coordinates and the interatomic distances were estimated (Lipson & Cochran, 1953) assuming $\sigma(F) \sim 0{\cdot}15|F|$, and $p = 5$ Å^{-2}. The standard deviations in bond angles were estimated by the method of Ahmed & Cruickshank (1953).

Description of the structure and discussion

(a) *Molecular structure*

The bond lengths and bond angles found in the α-ketobutyrate group are shown in Fig. 2 and listed in Table 3. The mean plane through the atoms O_1, O_3, C_1 and C_2 can be represented by the equation

$$-0{\cdot}960X - 3{\cdot}765Y + 2{\cdot}621Z + 2{\cdot}229 = 0\,,$$

where X, Y and Z are expressed in Å units and referred to the axes of the unit cell. The normal distances of the individual atoms from the mean plane are +0·054 Å for atoms O_1, O_3 and C_2 and −0·054 Å for C_1. The rest of the molecule is non-planar. The atoms O_2 and C_4 are 0·426 Å and 0·299 Å away respectively from the plane containing the atoms C_1, C_2 and C_3.

Table 3. *Intramolecular bond lengths and angles*

	Bond lengths		Bond angles
C_1–O_1	1·149 ± 0·034 Å	O_1–C_1–O_3	128·6 ± 2·2°
C_1–O_3	1·330 ± 0·034	O_1–C_1–C_2	123·0 ± 2·3
C_1–C_2	1·587 ± 0·038	O_3–C_1–C_2	106·5 ± 1·9
C_2–O_2	1·289 ± 0·034	C_1–C_2–C_3	127·2 ± 2·2
C_2–C_3	1·376 ± 0·038	C_1–C_2–O_2	109·0 ± 1·9
C_3–C_4	1·511 ± 0·038	C_3–C_2–O_2	120·8 ± 2·1
		C_2–C_3–C_4	118·6 ± 2·3

The observed bond lengths and angles show that sodium α-ketobutyrate is enolized to a great extent in the crystalline state. In the pure keto form, one would expect the C_2–C_3 bond length to be about 1·5 Å (the expected distance between two bonded carbon atoms in the sp^2 state and the sp^3 state respectively) and the C_2–O_2 bond length to be about 1·2 Å (the corresponding bond length in sodium pyruvate is 1·183 ± 0·040 Å). Further, the expected value of the angle C_2–C_3–C_4 is about 109·5° (the tetrahedral angle). In the pure enol form, however, the expected C_2–C_3 bond length is about 1·33 Å (the C=C bond length in ethylene) and the expected C_2–O_2 distance is about 1·42 Å, the normal C–O single bond length. Further, the angle C_2–C_3–C_4 is expected to have a value of about 120°. The observed bond lengths (1·376 ± 0·038 Å for C_2–C_3 bond and 1·289 ± 0·034 Å for C_2–O_2 bond) and the observed value of the angle C_2–C_3–C_4 (118·6 ± 2·3°) lie in between the expected values for the keto and the enol form, thereby indicating a large percentage of enolization of the compound. It is likely that the keto and the enol forms are randomly distributed in the crystal. This may be the reason for the larger observed B values for atoms O_2 and C_2 (Table 1). It is difficult to account for the larger B values of these atoms on the basis of rigid-body vibrations or oscillations of the molecule. Intramolecular vibrations are also not expected to be large enough to account for these B values.

The C_1–C_2 bond length (1·587 ± 0·038 Å) in sodium α-ketobutyrate is close to the corresponding bond length in sodium pyruvate (1·579 ± 0·045 Å). It is possible that this increase from the standard single-bond length (1·545 Å) is in both cases significant. Such increase in the C–C bond length has been observed by Chaudhuri & Hargreaves (1956) in the structure of bishydroxydurylmethane, where the C–C bond distance increases to 1·60 Å. Unusually long C–C bond lengths have also been reported by Kitaigorodskii (1949) in the structure of acenaphthene where the distance between two bonded methylene carbons comes out to be 1·64 Å, and by Lemaire & Livingstone (1950) in the structure of octafluorocyclobutane where the C–C bond length is found to lie between 1·57 and 1·62 Å. In each case, the increase in bond length is attributed to intramolecular strain.

(b) *Crystal structure*

The projections of the structure along the c and b axes are shown in Fig. 3 and 4 respectively. The

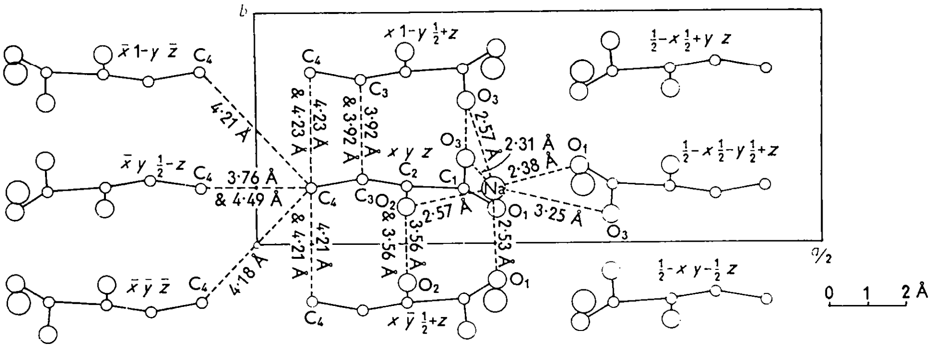

Fig. 3. Structure projected on (001).

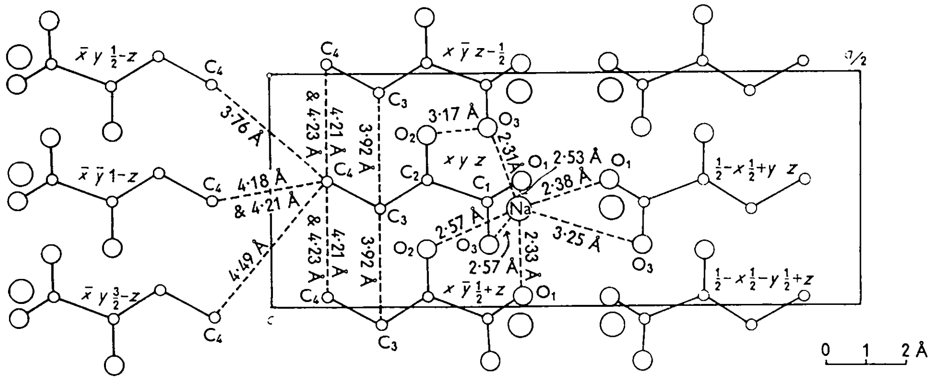

Fig. 4. Structure projected on (010).

Na–O bond lengths and the intermolecular distances are also indicated in these figures. This structure is quite similar to that of sodium pyruvate. In both, strong Na–O bonds tie the molecules into infinite layers parallel to the (100) plane; any one layer of molecules is linked with the neighbouring layers tightly on one side by Na–O bonds and loosely on the other side by van der Waals bonds. Similar arrangement of layers of molecules has also been observed in the crystal structures of potassium caprate (Vand, Lomer & Lang, 1949), potassium caproate (Lomer, 1952) and the potassium salt of *o*-nitrophenol hemihydrate (Richards, 1961).

In sodium α-ketobutyrate as well as in sodium pyruvate there are six short distances (2·5 ± 0·2 Å) between a sodium atom and the neighbouring oxygens; five of these oxygen atoms belong to the carboxylic groups while one atom belongs to the keto group. It seems plausible to assume that the close approach of the sodium atom to the keto group oxygen produces strain in the molecule and causes the lengthening of the C_1–C_2 bond.

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