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Acta Cryst. (1961). **14**, 1281

The Crystal Structure of Sodium Pyruvate*

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(*Received* 20 *February* 1961)

Sodium pyruvate, $CH_3COCOONa$, crystallized from aqueous solution, is monoclinic, space group $P2_1/a$, with four molecules per unit cell of dimensions

$$a = 22{\cdot}25,\ b = 5{\cdot}31,\ c = 3{\cdot}71\ \text{Å};\ \beta = 98{\cdot}2^\circ.$$

The detailed structure has been determined by two-dimensional Fourier syntheses, and refined by the method of least-squares.

The plane containing the methyl carbon, the keto group and the carbon of the carboxylic group makes an angle of 18·1° with the plane of the C–COO group. This suggests that there is no appreciable degree of conjugation across the central C–C bond, a fact that is confirmed by the observed central C–C bond length, $1{\cdot}579 \pm 0{\cdot}045$ Å, which is close to the standard single C–C bond length.

Strong Na–O bonds tie the molecules into infinite layers parallel to the (100) planes. Any one layer of molecules is linked with the neighbouring layers by strong Na–O bonds on one side and van der Waals bonds on the other.

Introduction

The α-keto acid analogs of amino acids are of considerable biochemical interest as intermediates in the biosynthesis and degradation of amino acids. They have unusual properties and are formed in the course of enzymatic oxidative deamination and transamination reactions. Although considerable work has been reported on the structure of amino acids, little attention has been given so far to the α-keto analogs. With a view to providing structural information which might throw light on their chemical characteristics, we have undertaken a programme to determine the structures of some of these compounds. In what follows, we report the structure analysis of the sodium salt of the simplest keto acid, i.e. pyruvic acid.

Experimental details

The crystals of sodium pyruvate were obtained from aqueous solution. They are monoclinic and grow as very thin plates, parallel to the (100) face. There is strong cleavage parallel to the plates. The crystal and physical data obtained are as follows:

$$a = 22{\cdot}25,\ b = 5{\cdot}31,\ c = 3{\cdot}71\ \text{Å};\ \beta = 98{\cdot}2^\circ.$$

The axial lengths were determined from the rotation photographs along the three axes, and the β angle from a Laue photograph, taken with X-rays, travelling parallel to the b axis.

The observed density at 25 °C., measured by the flotation method is 1·718 g.cm.$^{-3}$, and the calculated density for four molecules of $CH_3COCOONa$ per unit cell is 1·684 g.cm.$^{-3}$.

The systematic absences are: $0k0$ for k odd and $h0l$ for h odd, so that the space group is uniquely determined as $P2_1/a$. The linear absorption coefficient μ for Cu $K\alpha$ radiation is 23·7 cm.$^{-1}$. Reflexions of the type $hk0$, $h0l$ and $0kl$ were obtained from 10° or 15° oscillation photographs, using Cu $K\alpha$ radiation and the multiple-film technique. Of the 153 possible reflexions in the $hk0$ zone, 122 were observed while in the $h0l$ and $0kl$ zones, 93 and 19 reflexions were observed out of possible 105 and 27, respectively. The specimens used were flakes of roughly $(0{\cdot}7 \times 1{\cdot}1)$ mm.^{2} area. Intensities were measured visually, using intensity scales made with the same crystals. Corrections for Lorentz and polarization factors were applied and that for absorption was neglected. On account of the flakiness of the crystals, the shapes and sizes of the spots were not uniform, and this seems to be a serious source of error in the estimation of integrated intensities.

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

* Communication No. 445 from the National Chemical Laboratory, Poona-8, India.

stages of refinement. The final overall temperature factors for the three zones are: 1·1 Å^2 for $F(hk0)$, 2·1 Å^2 for $F(h0l)$ and 3·2 Å^2 for $F(0kl)$. 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 x and y coordinates of the sodium atom were obtained from the (001) Patterson projection. Signs of $F(hk0)$ were calculated on the basis of sodium positions alone, and an electron-density projection obtained. Assuming usual bond lengths and angles and a plane molecule nearly parallel to the plane of projection, a trial structure was then postulated and set up. This structure was refined by the usual iterative process till the structure factors stopped changing signs, except for a few small ones. At this stage, R was about 0·25. The coordinates were then refined twice by the method of least-squares. The maximum shift in coordinates after the final refinement was 0·03 Å. Four reflexions, whose F_o values were considered uncertain were not used in the final refinement. The final value of R was 0·220 on including all except very-high-angle unobserved reflexions at half the minimum observable value. On omitting the 200 reflexion, which appears to be subject to extinction, R decreased to 0·215. The (001) electron-density projection, shown in Fig. 1, was obtained using final calculated signs, and F_o values for all except 200, 110 and 510 reflexions. For these three reflexions, final F_c values were used.

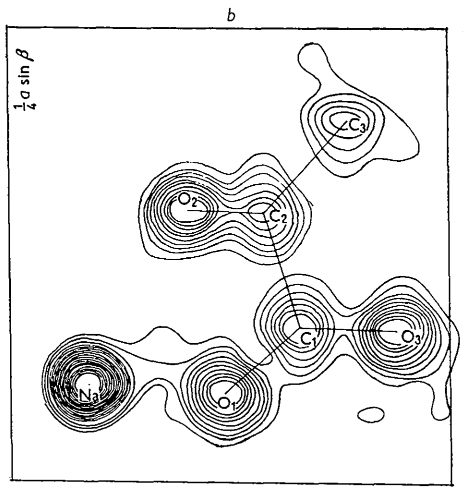

Fig. 1. Electron density projected on (001). Contours drawn at intervals of 1 e.Å^{-2}, starting from 2 e.Å^{-2}.

The (010) Patterson projection gave the approximate z coordinates of the sodium atom and the carboxylic oxygen atoms. The (010) electron-density projection was plotted on the basis of these atomic positions alone, and was refined by the usual method till the structure factors stopped changing signs, except for a few small ones. At this stage, R was about 0·3. The z coordinates were refined twice by the method of least-squares. Few coordinates, which were showing large shifts, were refined further till the maximum shift in coordinates was less than 0·02 Å. The final value of R was 0·223, which dropped to 0·192 on omitting 200, 201, 20$\bar{1}$, 10$\bar{2}$ and 202 reflexions. These five reflexions appear to be subject to extinction, and were not used in later refinements. The (010) electron-density projection, shown in Fig. 2, was obtained using final calculated signs, and F_o values for all except the five reflexions mentioned above, for which final F_c values were used.

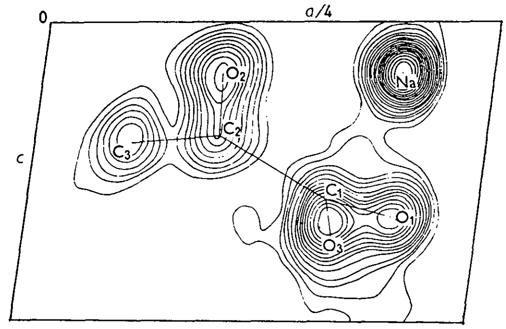

Fig. 2. Electron density projected on (010). Contours drawn at intervals of 1 e.Å^{-2}, starting from 2 e.Å^{-2}.

The R factor for $0kl$ reflexions was 0·210. The final atomic parameters are listed in Table 1, and the observed and calculated structure factors in Table 2.

Table 1. *Final atomic parameters*

	x/a	y/b	z/c
Na	0·1989 ± 0·0008	0·1802 ± 0·0032	0·1638 ± 0·0054
O_1	0·2035 ± 0·0010	0·4887 ± 0·0043	0·6491 ± 0·0073
O_2	0·1004 ± 0·0010	0·4100 ± 0·0043	0·1617 ± 0·0073
O_3	0·1707 ± 0·0010	0·8843 ± 0·0043	0·7144 ± 0·0073
C_1	0·1657 ± 0·0013	0·6608 ± 0·0057	0·5854 ± 0·0097
C_2	0·1024 ± 0·0013	0·5803 ± 0·0057	0·3685 ± 0·0097
C_3	0·0523 ± 0·0013	0·7722 ± 0·0057	0·3882 ± 0·0097

Estimation of errors

The standard deviations of atomic coordinates and the interatomic distances were estimated (Lipson & Cochran, 1953) assuming $\sigma(F) = 0{\cdot}2|F|$, and $p = 5$ Å^{-2}. A root mean square of $\sigma(x)$, $\sigma(y)$ and $\sigma(z)$ was taken as the standard deviation of each atomic position.

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 pyruvate group are shown in Fig. 3 and listed in Table 3. The mean plane through the atoms C_2, C_1, O_1 and O_3 can be represented by the equation

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
2 0 0	36	-52	23 2 0	8	7	13 5 0	9	-10	$\bar{5}$ 0 2	26	-27
4 0 0	38	-38	24 2 0	5	-3	14 5 0	9	-13	$\bar{6}$ 0 2	19	23
6 0 0	30	20	25 2 0	4	5	15 5 0	<3	1	$\bar{7}$ 0 2	<3	-1
8 0 0	77	-65	26 2 0	5	-4	16 5 0	4	5	$\bar{8}$ 0 2	14	16
10 0 0	63	56	1 3 0	9	-14	17 5 0	4	-4	$\bar{9}$ 0 2	7	-6
12 0 0	18	-11	2 3 0	6	3	18 5 0	4	-3	$\bar{10}$ 0 2	5	-2
14 0 0	22	-21	3 3 0	21	30	19 5 0	4	7	$\bar{11}$ 0 2	<5	2
16 0 0	12	-7	4 3 0	20	-27	0 6 0	3	3	$\bar{12}$ 0 2	11	-11
18 0 0	7	7	5 3 0	32	-40	1 6 0	<6	-6	$\bar{13}$ 0 2	12	12
20 0 0	30	29	6 3 0	<3	0	2 6 0	15	-18	0 0 3	<3	-4
22 0 0	18	-13	7 3 0	34	32	3 6 0	<6	3	1 0 3	7	-4
24 0 0	8	5	8 3 0	7	9	4 6 0	8	10	2 0 3	9	-7
26 0 0	12	-11	9 3 0	8	-7	5 6 0	<3	7	3 0 3	5	2
28 0 0	8	-8	10 3 0	8	-9	6 6 0	11	14	4 0 3	<4	1
1 1 0	16	-29	11 3 0	3	-6	7 6 0	<3	-2	5 0 3	9	-9
2 1 0	13	15	12 3 0	3	4	8 6 0	10	-11	6 0 3	5	2
3 1 0	11	13	13 3 0	19	23	9 6 0	<3	5	7 0 3	<5	2
4 1 0	17	17	14 3 0	<2	6	10 6 0	4	4	8 0 3	4	4
5 1 0	20	34	15 3 0	21	-25	11 6 0	<3	-2	9 0 3	9	7
6 1 0	12	-12	16 3 0	<2	-1	12 6 0	9	-7	$\bar{1}$ 0 3	7	8
7 1 0	18	19	17 3 0	15	14	13 6 0	6	-8	$\bar{2}$ 0 3	4	7
8 1 0	48	50	18 3 0	5	6	0 0 1	30	-32	$\bar{3}$ 0 3	<4	5
9 1 0	40	-40	19 3 0	4	-5	1 0 1	18	-18	$\bar{4}$ 0 3	<4	-1
10 1 0	18	-20	20 3 0	5	2	2 0 1	28	-44	$\bar{5}$ 0 3	12	-15
11 1 0	15	-9	21 3 0	4	-6	3 0 1	11	-7	$\bar{6}$ 0 3	5	6
12 1 0	28	-23	22 3 0	7	-7	4 0 1	42	49	$\bar{7}$ 0 3	8	-2
13 1 0	10	8	23 3 0	8	9	5 0 1	5	3	$\bar{8}$ 0 3	7	-9
14 1 0	31	22	24 3 0	6	-4	6 0 1	23	-23	$\bar{9}$ 0 3	14	9
15 1 0	18	10	25 3 0	8	-9	7 0 1	18	17	$\bar{10}$ 0 3	8	-7
16 1 0	28	-33	0 4 0	20	-11	8 0 1	5	-3	$\bar{11}$ 0 3	7	4
17 1 0	16	13	1 4 0	21	28	9 0 1	5	-1	$\bar{12}$ 0 3	4	11
18 1 0	17	11	2 4 0	<9	3	10 0 1	8	8	0 0 4	17	-15
19 1 0	18	-17	3 4 0	11	-14	11 0 1	23	-18	1 0 4	11	10
20 1 0	18	11	4 4 0	19	19	12 0 1	7	-3	2 0 4	7	-5
21 1 0	7	-6	5 4 0	8	-9	13 0 1	7	9	3 0 4	8	11
22 1 0	14	-13	6 4 0	8	-8	$\bar{1}$ 0 1	12	17	4 0 4	3	-2
23 1 0	5	6	7 4 0	16	14	$\bar{2}$ 0 1	36	54	5 0 4	8	-10
24 1 0	15	14	8 4 0	<3	-4	$\bar{3}$ 0 1	14	-17	$\bar{1}$ 0 4	8	-7
25 1 0	5	5	9 4 0	17	-20	$\bar{4}$ 0 1	31	-31	$\bar{2}$ 0 4	8	8
26 1 0	<4	0	10 4 0	5	-3	$\bar{5}$ 0 1	34	36	$\bar{3}$ 0 4	7	-5
27 1 0	4	2	11 4 0	11	13	$\bar{6}$ 0 1	15	14	$\bar{4}$ 0 4	12	12
0 2 0	4	3	12 4 0	16	-21	$\bar{7}$ 0 1	11	-14	$\bar{5}$ 0 4	7	-8
1 2 0	<6	-6	13 4 0	<3	1	$\bar{8}$ 0 1	12	9	$\bar{6}$ 0 4	<4	0
2 2 0	8	-7	14 4 0	10	15	$\bar{9}$ 0 1	24	-27	$\bar{7}$ 0 4	7	7
3 2 0	16	20	15 4 0	<3	2	$\bar{10}$ 0 1	7	-5	$\bar{8}$ 0 4	4	-2
4 2 0	9	-10	16 4 0	5	8	$\bar{11}$ 0 1	15	21	0 1 1	37	-41
5 2 0	<3	-2	17 4 0	4	5	$\bar{12}$ 0 1	7	-6	0 2 1	10	-7
6 2 0	13	-13	18 4 0	11	-8	$\bar{13}$ 0 1	<4	1	0 3 1	12	-12
7 2 0	8	-8	19 4 0	9	-8	0 0 2	26	-30	0 4 1	3	-5
8 2 0	16	17	20 4 0	4	6	1 0 2	14	-14	0 5 1	17	10
9 2 0	8	9	21 4 0	9	7	2 0 2	39	51	0 6 1	<2	-1
10 2 0	16	21	22 4 0	3	-1	3 0 2	24	-27	0 1 2	25	-26
11 2 0	18	-16	1 5 0	<10	10	4 0 2	23	25	0 2 2	<2	-4
12 2 0	2	4	2 5 0	<10	-1	5 0 2	9	-8	0 3 2	<3	-2
13 2 0	15	17	3 5 0	<10	4	6 0 2	12	-15	0 4 2	10	5
14 2 0	<3	-3	4 5 0	7	7	7 0 2	9	8	0 5 2	9	-6
15 2 0	5	-4	5 5 0	12	-14	8 0 2	18	-11	0 6 2	<2	1
16 2 0	14	-12	6 5 0	8	8	9 0 2	15	9	0 1 3	3	3
17 2 0	16	-12	7 5 0	10	-10	10 0 2	14	-6	0 2 3	9	9
18 2 0	<3	1	8 5 0	7	-7	11 0 2	5	4	0 3 3	3	2
19 2 0	15	11	9 5 0	12	12	$\bar{1}$ 0 2	35	52	0 4 3	3	4
20 2 0	<3	-1	10 5 0	6	6	$\bar{2}$ 0 2	38	-47	0 5 3	<2	4
21 2 0	13	-10	11 5 0	4	3	$\bar{3}$ 0 2	14	16	0 1 4	6	5
22 2 0	5	-2	12 5 0	<3	1	$\bar{4}$ 0 2	7	-4	0 2 4	<2	-1
									0 3 4	<2	1

$$1\cdot6813x'+1\cdot2912y-4\cdot3267z'-3\cdot4032=0\ ,$$

where x', y and z' are expressed in Å units and referred to the orthogonal axes a', b and c. The perpendicular distances of the individual atoms from the mean plane are 0·029 Å for O_1, C_2 and O_3 and $-0\cdot029$ Å for C_1.

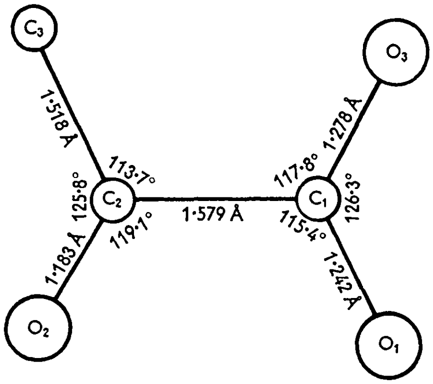

Fig. 3. Bond lengths and bond angles in the pyruvate group. O_1 and O_3 are carboxylic oxygens, O_2 is keto group oxygen and C_3 is methyl carbon.

Referred to the same axes a', b and c, the mean plane through the atoms C_1, C_2, O_2 and C_3 can be represented by the equation

$$1\cdot3021x'+2\cdot8726y-4\cdot1758z'-7\cdot6983=0\ .$$

The perpendicular distances of the individual atoms from the mean plane are 0·050 Å for O_2, C_1 and C_3 and $-0\cdot050$ Å for C_2.

The two planes make an angle of 18·1° with each other.

Table 3. *Intramolecular bond lengths and angles*

	Bond length		Bond angles
C_1–O_1	1·242 ± 0·040 Å	O_1–C_1–O_3	126·3 ± 2·5°
C_1–O_3	1·278 ± 0·040	O_1–C_1–C_2	115·4 ± 2·4
C_1–C_2	1·579 ± 0·045	O_3–C_1–C_2	117·8 ± 2·4
C_2–O_2	1·183 ± 0·040	C_1–C_2–O_2	119·1 ± 2·5
C_2–C_3	1·518 ± 0·045	C_1–C_2–C_3	113·7 ± 2·3
		O_2–C_2–C_3	125·8 ± 2·6

The central C_1–C_2 bond length (1·579 ± 0·045 Å) is not significantly different from the normal single C–C bond length. This suggests that there is no appreciable

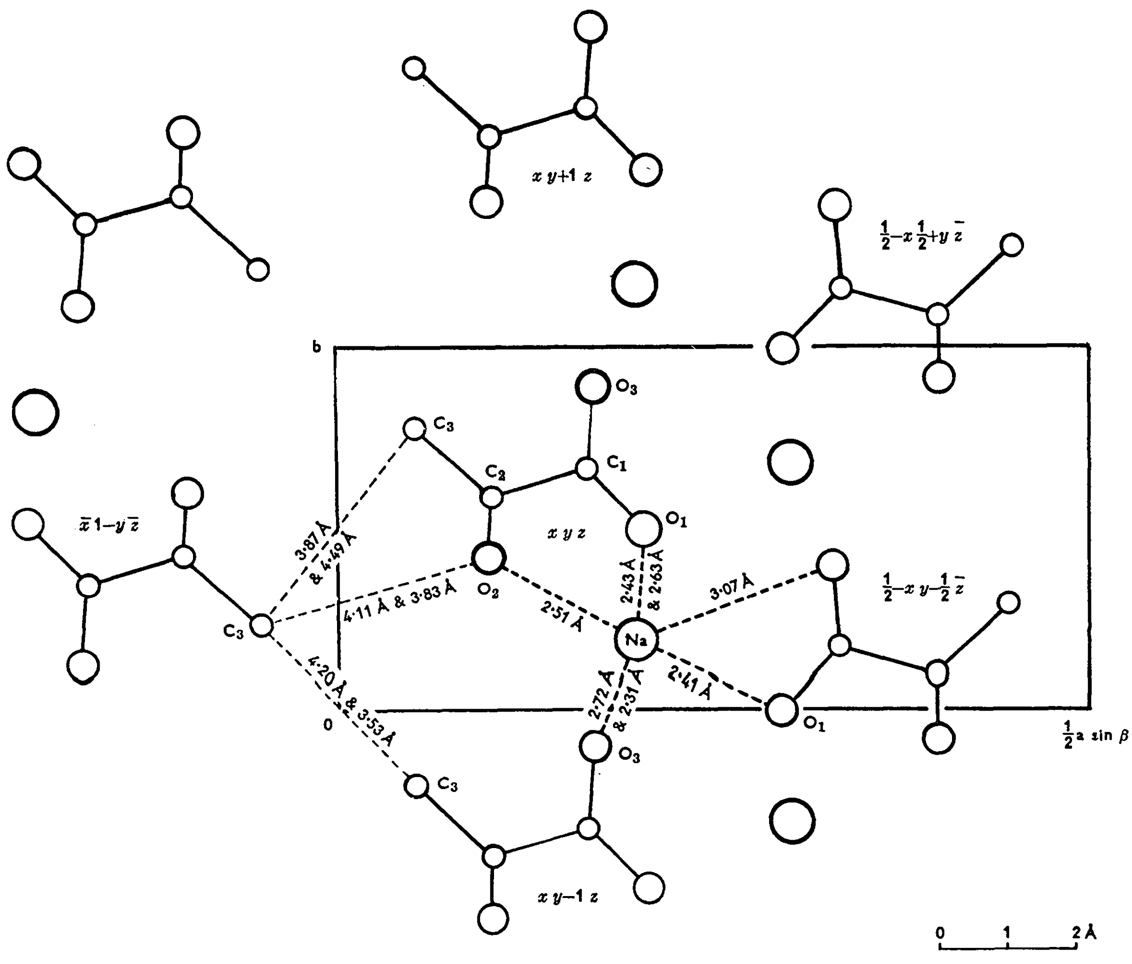

Fig. 4. Structure projected on (001).

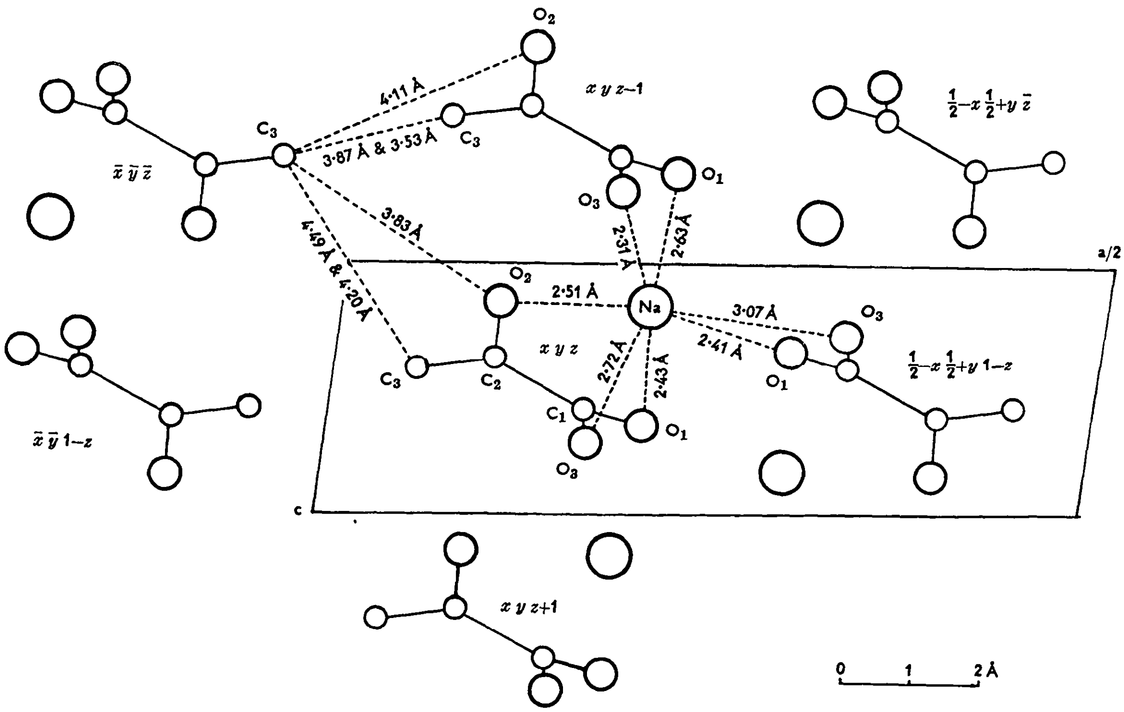

Fig. 5. Structure projected on (010).

degree of conjugation across this bond. There would thus be a possibility of free rotation of the two planes across the central C–C bond. This explains the fact that the two planes $C_1C_2O_2C_3$ and $C_2C_1O_3O_1$ are not coplanar but make an angle of 18·1° with each other.

The two bonds C_1–O_1 and C_1–O_3 are of different lengths, although the difference may be within experimental error. In oxalic acid and eight amino-acids listed by Ahmed & Cruickshank (1953), the two C–O bonds are always of unequal lengths.

The angle O_1–C_1–O_3 (126·3 ± 2·5°) is significantly larger than the angles C_2–C_1–O_1 (115·4 ± 2·4°) and C_2–C_1–O_3 (117·8 ± 2·4°). This is in agreement with the results found for oxalic acid and the amino-acids listed by Ahmed & Cruickshank (1953).

The differences in the angles O_2–C_2–C_3 (125·8 ± 2·6°), O_2–C_2–C_1 (119·1 ± 2·5°) and C_3–C_2–C_1 (113·7 ± 2·3°) are also significant.

On account of the rather large uncertainties in the observed bond lengths and angles, a discussion of the molecular structure with reference to its chemical properties or to the molecular structures of related compounds is not warranted at this stage.

(*b*) *Crystal structure*

The projections of the structure along the *c* and *b* axes are shown in Fig. 4 and 5 respectively.

There are six short bonds and one slightly longer bond between Na(x, y, z) and the neighbouring oxygens; these distances are as follows:

Na–$O_1(x, y, z)$	2·43 ± 0·03 Å
Na–$O_1(x, y, z-1)$	2·63 ± 0·03
Na–$O_3(x, y-1, z)$	2·72 ± 0·03
Na–$O_3(x, y-1, z-1)$	2·31 ± 0·03
Na–$O_1(\frac{1}{2}-x, y-\frac{1}{2}, 1-z)$	2·41 ± 0·03
Na–$O_2(x, y, z)$	2·51 ± 0·03
Na–$O_3(\frac{1}{2}-x, y-\frac{1}{2}, 1-z)$	3·07 ± 0·03

There are van der Waals bonds between the methyl carbons C_3 and keto group oxygens O_2, and between carbons and carbons of the neighbouring molecules. The more significant distances are as follows:

$C_3(\bar{x}, 1-y, \bar{z})$–$C_3(x, y, z)$	4·49 ± 0·06 Å
$C_3(\bar{x}, 1-y, \bar{z})$–$C_3(x, y, z-1)$	3·87 ± 0·06
$C_3(\bar{x}, 1-y, \bar{z})$–$C_3(x, y-1, z)$	4·20 ± 0·06
$C_3(\bar{x}, 1-y, \bar{z})$–$C_3(x, y-1, z-1)$	3·53 ± 0·06
$C_3(\bar{x}, 1-y, \bar{z})$–$O_2(x, y, z-1)$	4·11 ± 0·04
$C_3(\bar{x}, 1-y, \bar{z})$–$O_2(x, y, z)$	3·83 ± 0·04

The strong Na–O bonds tie the molecules into infinite layers parallel to the (100) plane. Anyone layer of molecules is linked with the neighbouring layers tightly on one side by bonds such as Na(x, y, z)–$O_1(\frac{1}{2}-x, y-\frac{1}{2}, 1-z)$, and loosely on the other side by van der Waals bonds, mentioned above. This arrangement explains the presence of strong cleavage parallel to the (100) face.

The refinement of the temperature factors has not been attempted. The differences in the overall temperature factors for the three projections, however, suggest that the mean amplitude of the thermal vibration of atoms has the largest component along the *c* axis and the smallest component along the *a* axis, since the overall temperature factor is least for the (001) projection (1·1 Å^2) and maximum for the (100) projection (3·2 Å^2). This is also indicated by the (010) electron-density projection (Fig. 2) where the atomic contours, especially those of the methyl carbon atom, appear distinctly elongated nearly along the *c* axis. This can be understood from the orientation of the molecule (x, y, z) with respect to the neighbouring molecules in Fig. 4. The atom O_1 is strongly bonded to the two sodium atoms (x, y, z) and $(x, y, z+1)$, and atom O_3 is strongly bonded to the two sodium atoms $(x, y+1, z)$ and $(x, y+1, z+1)$. The methyl carbon C_3 and keto-group oxygen O_2 are bonded to the neighbouring molecules by weak forces only. The oscillation of the molecule about the line O_1–O_3 should therefore be most likely, and so the components of the thermal vibration amplitudes of the atoms C_2, C_3 and O_2 will be maximum along the *c* axis and will be least along the *a* axis. The bond between Na(x,y,z) and $O_2(x,y,z)$ is quite strong (distance –2·51 Å), but since the movement of the atom O_2 would take place nearly perpendicular to the Na–O_2 bond, the Na–O_2 distance is not expected to alter appreciably during the oscillation. Besides, there is a possibility of free rotation about the central C–C bond, so that the plane C_3–C_2–O_2 may keep turning suitably during the oscillation so that the Na–O_2 distance is not affected.

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Short Communications

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Acta Cryst. (1961). **14**, 1286

A note on the crystal structure of zirconium pyrophosphate.

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(*Received* 26 *June* 1961)

Levi & Peyronel's (1935) structure of zirconium pyrophosphate ZrP_2O_7 requires that the central P–O–P group of the pyrophosphate ion be linear, lying in fact on a three-fold axis. In both paper and abstract there occurs an unfortunate numerical error by which the P–P distance is incorrectly given as 3·03 Å which is less than twice 1·56 Å, the P–O distance. This has led some writers (Hanwick & Hoffmann, 1951; Van Wazer, 1958) to the conclusion that the P–O–P angle is 152° and not 180°. Furthermore it has been felt that since the X-ray scattering is dominated by the zirconium atoms, the determination of the structure of the pyrophosphate ion may not be unequivocal.

The low temperature form of ZrP_2O_7 crystallizes in a primitive cubic cell of side $a_0 = 8·258$ Å (Harrison, McKinstry & Hummel, 1954). Levi & Peyronel give the density as about 3·3 g.cm.$^{-3}$, which corresponds to four formula units per cell. In any such cell at least some of the eight phosphorus atoms must lie on three-fold axes. If $P_2O_7^{4-}$ is a discrete ion and one phosphorus atom lies on a three-fold axis, so must the other, for otherwise the ion would contain four phosphorus atoms; the only sensible way of distributing the seven oxygen atoms is to place one on the axis and six in two symmetrical groups of three. To preserve four-fold grouping of oxygen atoms round the phosphorus atoms the only possible configuration is one in which the single oxygen atom is placed on the three-fold axis between the phosphorus atoms.

The existence and linearity of the central P–O–P group in ZrP_2O_7 can thus be confirmed (without detailed knowledge of the structure or even the space group) from considerations of the Bravais lattice, cell size and density, and the assumption that the P_2O_7 ion is discrete. It should be noted, however, that in $Na_4P_2O_7.10H_2O$ the P–O–P angle is 134° (MacArthur & Beevers, 1957).

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