

in good agreement with the value of 1.477 Å quoted by Cruickshank & Sparks (1960) for the (sp^2) single-bond length between trigonally linked carbon atoms and do not differ significantly from the values obtained for other halogen substituted biphenyls.

The O(1)–C(13) and O(2)–C(13) bond lengths of 1.246 ± 0.015 and 1.283 ± 0.015 Å were respectively longer and shorter than had been expected. The bond lengths are similar to those obtained in 2'-iodobiphenyl-4-carboxylic acid of 1.261 ± 0.010 and 1.289 ± 0.010 Å respectively.

The O–H...O bond of 2.61 Å which is the shortest intermolecular distance, is similar to the value quoted

for 2'-iodobiphenyl-4-carboxylic acid of 2.60 Å. The bond angles C(10)–C(13)–O(1)–C(10)–C(13)–O(2) and O(1)–C(13)–O(2) are comparable with those found in similar compounds.

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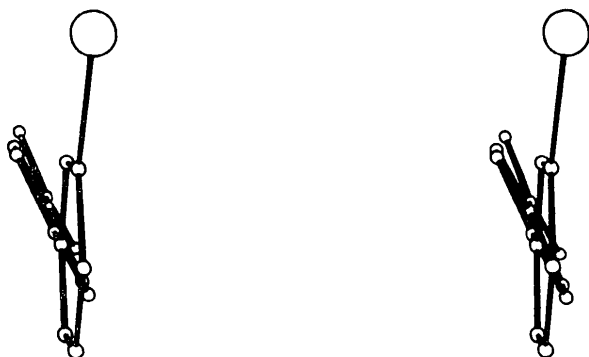


Fig. 2. A stereo view of 3'-iodobiphenyl-4-carboxylic acid.

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The Crystal and Molecular Structure of Potassium Hydrogen DL-Methylsuccinate

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The structure of potassium hydrogen DL-methylsuccinate [$\text{KO}_2\text{C}\cdot\text{CH}(\text{CH}_3)\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$] was determined from three-dimensional X-ray data. The crystals are monoclinic with $a=11.927$, $b=6.217$, $c=9.731$ Å, $\beta=105.65^\circ$, $Z=4$, space group $P2_1/c$. The structure was solved by direct methods and was refined by a block-diagonal least-squares procedure to $R=0.040$. The succinic acid skeleton of the acid methylsuccinate ion is bent. The short intermolecular hydrogen bond with O(H)...O distance of 2.543(3) Å is acentric.

Introduction

We started this investigation because we were interested in the molecular conformation of the acid DL-methylsuccinate ion and in the intermolecular hydrogen bonding of acid salts of carboxylic acids in general.

In addition, knowledge of the molecular conformation might be helpful to our interpretation of the

Patterson synthesis of DL-methylsuccinic acid, the structure of which has proved to be difficult to determine because of poor crystals and the lack of reliable data.

Experimental

Crystals of potassium hydrogen DL-methylsuccinate were obtained by the slow evaporation, at room

temperature, of an aqueous solution of stoichiometric quantities of DL-methylsuccinic acid and potassium carbonate.

The unit-cell dimensions were calculated from 24 reflexions ($2\theta < 70^\circ$) measured on a Nonius automatic three-circle diffractometer AD3 with Cu $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) and were refined by least-squares methods (van den Berg & Rutten-Keulemans, 1963). The values obtained were:

$$a = 11.927 (2) \quad b = 6.217 (2) \quad c = 9.731 (2) \text{ \AA} \\ \beta = 105.65 (3)^\circ \quad V = 695 \text{ \AA}^3.$$

From Weissenberg photographs the extinctions $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ were found; the space group is $P2_1/c$. With $Z = 4$ the calculated density is 1.62 g.cm^{-3} ; the density measured by flotation is 1.64 g.cm^{-3} .

Integrated intensities of 1296 independent reflexions ($2\theta < 140^\circ$) were measured on the diffractometer with Ni-filtered Cu radiation. The diffractometer is equipped with a scintillation counter, a discriminator, and an automatic filter disc. The ω -scanning technique was used and the scanning range was adjusted to the width of the peaks.

The intensities were corrected for Lorentz and

Table 1. *Final fractional atomic coordinates with estimated standard deviations in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>
K	0.48760 (5)	0.23074 (9)	0.13527 (6)
O(1)	0.3338 (1)	0.5463 (3)	0.1565 (2)
O(2)	0.3916 (2)	0.8379 (3)	0.0654 (2)
O(3)	0.3465 (2)	0.3967 (3)	-0.1595 (2)
O(4)	0.1934 (2)	0.1898 (3)	-0.2555 (2)
C(1)	0.3191 (2)	0.6934 (4)	0.0628 (3)
C(2)	0.2062 (2)	0.6969 (4)	-0.0567 (3)
C(3)	0.1627 (2)	0.4765 (4)	-0.1135 (3)
C(4)	0.2444 (2)	0.3534 (4)	-0.1781 (3)
C(5)	0.1130 (3)	0.8125 (6)	-0.0023 (4)
H(1)	0.220 (2)	0.790 (5)	-0.130 (3)
H(2)	0.141 (3)	0.961 (6)	0.027 (4)
H(3)	0.095 (3)	0.728 (6)	0.081 (4)
H(4)	0.035 (3)	0.815 (6)	-0.080 (4)
H(5)	0.078 (2)	0.489 (5)	-0.184 (3)
H(6)	0.153 (3)	0.384 (6)	-0.029 (3)
H(7)	0.252 (3)	0.104 (6)	-0.297 (4)

Table 2. *Final thermal parameters with estimated standard deviations in parentheses*

The β_{ij} coefficients are given by

$$\exp [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{23} + 2lh\beta_{31})].$$

	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{23}$	$2\beta_{31}$
K	0.00489 (4)	0.01453 (14)	0.00683 (6)	0.0008 (1)	0.0001 (1)	0.0022 (1)
O(1)	0.0055 (1)	0.0168 (5)	0.0069 (2)	-0.0008 (4)	0.0053 (5)	0.0011 (3)
O(2)	0.0064 (2)	0.0180 (5)	0.0093 (2)	-0.0055 (5)	-0.0006 (6)	0.0039 (3)
O(3)	0.0055 (2)	0.0253 (6)	0.0121 (3)	-0.0030 (5)	-0.0114 (7)	0.0053 (3)
O(4)	0.0062 (2)	0.0209 (6)	0.0115 (3)	-0.0010 (5)	-0.0108 (6)	0.0028 (3)
C(1)	0.0047 (2)	0.0136 (6)	0.0068 (3)	0.0006 (6)	-0.0019 (7)	0.0032 (4)
C(2)	0.0055 (2)	0.0176 (7)	0.0069 (3)	0.0026 (6)	0.0000 (7)	0.0014 (4)
C(3)	0.0049 (2)	0.0204 (8)	0.0077 (3)	-0.0004 (6)	-0.0049 (8)	0.0013 (4)
C(4)	0.0054 (2)	0.0172 (7)	0.0068 (3)	-0.0001 (6)	0.0001 (7)	0.0018 (4)
C(5)	0.0065 (2)	0.0285 (10)	0.0135 (4)	0.0089 (8)	-0.0087 (11)	0.0015 (5)

polarization factors, and an absorption correction was applied, the linear absorption factor being 63 cm^{-1} for Cu $K\alpha$ radiation. The crystal was a parallelepiped of $0.28 \times 0.22 \times 0.10 \text{ mm}$ which was adjusted along the reciprocal $(\bar{1}04)$ axis.

Structure determination

An overall temperature factor ($B = 3.5 \text{ \AA}^2$) and scaling factor were determined by Wilson's (1942) method and normalized structure factors were calculated.

Signs for reflexions with $E > 1.3$ were determined by using a symbolic method (Spek, 1972) which yielded eight solutions. For each solution a reliability index, c , was evaluated, where:

$$c = \sum_{h,k} s_h s_k s_{h+k} |E_h E_k E_{h+k}|$$

The E map corresponding to the solution with the highest value of c revealed the ten non-hydrogen atoms.

Refinement of the structure

The structure was refined by block-diagonal least-squares methods. The atomic form factors were taken from Moore (1963). All 1296 reflexions were included in the refinement and were given unit weight. The non-hydrogen model was refined with isotropic thermal parameters to $R = 0.089$. Introduction of anisotropic thermal parameters reduced R to 0.059. A difference Fourier synthesis revealed the seven hydrogen atoms. The disagreement index decreased to 0.043 after several cycles of refinement with anisotropic thermal parameters for K⁺, C and O and with an isotropic thermal parameter of 3.5 \AA^2 for all hydrogen atoms.

As some reflexions suffered strongly from extinction, a least-squares extinction-parameter refinement (Zachariasen 1967, 1968) was carried out, which lowered R to 0.040; the extinction parameter, defined as $r^*(e^2/mc^2)^2 \lambda^2 / V^2$, is $3.9 \times 10^{-3} \text{ cm}^{-1}$.

A final difference Fourier map showed no peaks higher than 0.25 e.\AA^{-3} . The final coordinates and thermal parameters are listed in Tables 1 and 2

ionized carboxyl group, 1.313 and 1.213 Å. These values are in good agreement with those found in potassium hydrogen *meso*-tartrate (Kroon & Kanters, 1972), in the 1:1 addition compound of ammonium acetate and acetic acid (Nahringbauer, 1969), and in potassium hydrogen di-*p*-nitrobenzoate (Shrivastava & Speakman, 1961).

The methyl group is in the α position with respect to the ionized carboxyl group. C(2), C(1), O(1) and O(2) are in one plane; the average deviation from planarity is less than 0.004 Å. C(3), C(4), O(3) and O(4) are also coplanar with an average deviation of less than 0.003 Å.

The carbon chain C(1)~C(4) is bent, but C(4), C(3), C(2) and C(5) are roughly coplanar with an average deviation of 0.02 Å, resulting in a staggered conformation around the bond C(2)–C(3). The methyl group is not in the C(2)C(1)O(1)O(2) plane; the angle between the C(2)C(1)O(1)O(2) and C(1)C(2)C(5) planes is 86.1°.

The two C–C bond lengths in which a carbon atom of a carboxyl group participates differ significantly; the shorter one involves the carbon atom of the non-ionized carboxyl group. This effect was also found in L-aspartic acid (Derissen, Endeman & Peerdeman, 1968) and in aminomalonic acid (Kanters, Kroon, Beurskens & Vliegthart, 1966).

Crystal structure

We can distinguish three layers parallel to the (100) plane, two of them containing DL-methylsuccinate ions, the third K⁺ ions. The two methylsuccinate layers are related by a centre of inversion (Fig. 2).

The methylsuccinate layers consist of zigzag chains. The ions in the chain are linked by a short intermole-

cular hydrogen bond [2.543 (3) Å] and the chains are fixed in a three-dimensional network by K⁺...O interactions. Thus all three layers are linked, forming a 'superlayer' with K⁺ in the central layer. The 'superlayers' are linked only by van der Waals interactions; the methyl groups of one 'superlayer' are directed towards the methyl groups of the next 'superlayer'.

The potassium–oxygen interactions can be divided into:

(1) interactions with distances ranging from 2.705 to 2.763 Å; the oxygen atoms involved belong to ionized carboxyl groups. Each potassium ion participates in four such interactions, forming a distorted tetrahedron

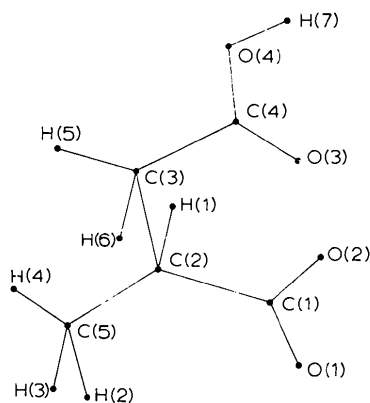


Fig. 1. The structure of the acid methylsuccinate ion.

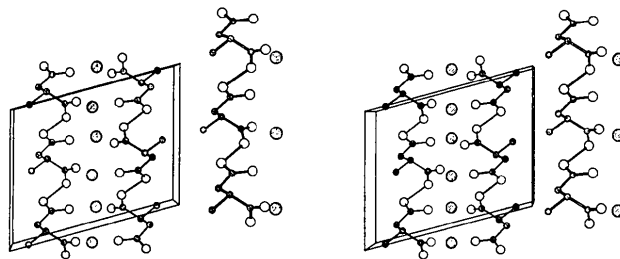


Fig. 2. A stereoscopic view of the crystal structure along [010]. Hydrogen atoms are not included. The potassium ions are shaded, the carbon atoms dotted.

Table 4. Bond lengths with estimated standard deviations in parentheses

C(1)–O(1)	1.270 (3) Å	C(2)–H(1)	0.97 (3) Å
C(1)–O(2)	1.242 (3)	C(5)–H(2)	1.00 (4)
C(4)–O(3)	1.213 (3)	C(5)–H(3)	1.04 (4)
C(4)–O(4)	1.313 (3)	C(5)–H(4)	1.03 (3)
C(1)–C(2)	1.524 (4)	C(3)–H(5)	1.06 (3)
C(2)–C(3)	1.516 (4)	C(3)–H(6)	1.04 (4)
C(3)–C(4)	1.504 (4)	O(4)–H(7)	1.05 (4)
C(2)–C(5)	1.533 (4)		

Table 5. Bond angles with estimated standard deviations in parentheses

O(1)–C(1)–O(2)	123.0 (0.2)	C(1)–C(2)–H(1)	106.4 (1.6)
O(3)–C(4)–O(4)	123.3 (0.2)	C(2)–C(5)–H(2)	108.0 (1.5)
C(2)–C(1)–O(1)	118.7 (0.2)	C(2)–C(5)–H(3)	104.0 (1.6)
C(2)–C(1)–O(2)	118.2 (0.2)	C(2)–C(5)–H(4)	110.5 (1.5)
C(3)–C(4)–O(3)	124.3 (0.2)	C(3)–C(2)–H(1)	112.5 (1.6)
C(3)–C(4)–O(4)	112.4 (0.2)	C(2)–C(3)–H(5)	110.0 (1.5)
C(1)–C(2)–C(3)	114.2 (0.2)	C(4)–C(3)–H(5)	112.2 (1.5)
C(1)–C(2)–C(5)	108.5 (0.2)	C(4)–C(3)–H(6)	106.1 (1.6)
C(5)–C(2)–C(3)	109.9 (0.2)	C(4)–O(4)–H(7)	111.1 (1.8)
C(2)–C(3)–C(4)	114.5 (0.2)	C(2)–C(3)–H(6)	108.3 (1.5)
		H(2)–C(5)–H(3)	112.0 (3.0)
		H(2)–C(5)–H(4)	111.5 (2.8)
		H(3)–C(5)–H(4)	104.0 (3.0)

of oxygen atoms around the central potassium ion (Fig. 3 and Table 6).

(2) four weaker interactions, in which the distances range from 2.956 to 3.085 Å. In one interaction (2.956 Å) the oxygen atom involved belongs to an ionized carboxyl group; double-bonded oxygen atoms participate in the other interactions. This effect results in an asymmetrical arrangement of four oxygen atoms with respect to the potassium ion.

All other $K^+ \cdots O$ distances are greater than 3.4 Å. Short intermolecular distances are shown in Table 7.

Table 6. *The oxygen-potassium-oxygen angles of the distorted tetrahedron composed of a central potassium ion and four 'short distance' oxygen atoms*

(See Fig. 3 for key to transformations.)

O(1)-K-O(2)	114.8°	O(2)-K-O(1''')	90.0°
O(1)-K-O(1''')	130.1	O(2)-K-O(2'')	87.1
O(1)-K-O(2'')	130.9	O(1''')-K-O(2'')	90.5

Table 7. *Short intermolecular distances with estimated standard deviations in parentheses*

(See Fig. 3 for key to transformations.)

O(4)-H(6')	2.61 (3) Å	H(6)-H(7')	2.25 (5) Å
H(4)-H(2'')	2.69 (5)	H(5)-H(4''')	2.56 (4)
H(3)-H(5'')	2.85 (5)	H(4)-H(6'')	2.99 (5)

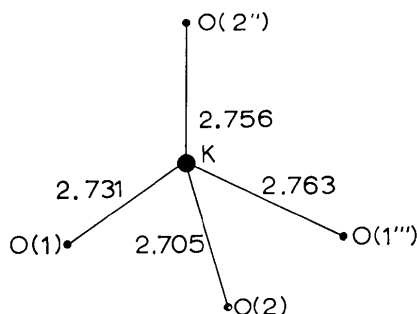


Fig. 3. The environment of the potassium ion including oxygen atoms at short distances. The oxygen atoms of the molecule corresponding to the coordinates in Table 1, are unprimed. The symmetry related atoms are designated as follows: (') $x - y + 0.5z + 0.5$; (') $-x - y - z$; (''') $-x y + 0.5 - z + 0.5$.

Intermolecular hydrogen bond

The intermolecular hydrogen bond is acentric [*B*-type according to Shrivastava & Speakman (1961)]. The $O(H) \cdots O$ distance is 2.543 (3) Å, in good agreement with values found in rubidium hydrogen bisglycollate (Golič & Speakman, 1965), in sodium hydrogen fumarate (Gupta & Sahu, 1970), in potassium hydrogen *meso*-tartrate (Kroon & Kanters, 1972) and in potassium hydrogen oxalate (Pedersen, 1968). This hydrogen atom is coplanar with the non-ionized carboxyl group; the deviation of the hydrogen atom from the plane is 0.02 Å, which is less than the corresponding standard deviation. The oxygen atom of the ionized carboxyl group, participating in the hydrogen bond, is 0.25 Å out of this plane. The deviation from linearity in this bond is about 2°, a value close to the standard deviation.

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