Tableau 9. *Les liaisons C–O et C–C adjacente dans les ions oxocarbonium*

Composés	C–O	C–C
$[CH_3CO]^+$ $[SbF_6]^-$	1,108 (15) Å	1,385 (16) Å
$[CH_3CO]^+$ $[SbCl_6]^-$	1,109 (24)	1,452 (30)
$[CH_3-CH_2CO]^+$ $[GaCl_4]^-$	1,099 (20)	1,435 (24)
$[(CH_3)_2-CHCO]^+$ $[SbCl_6]^-$	1,116 (10)	1,439 (12)
$[CH_3-2-C_6H_4CO]^+$ $[SbCl_6]^-$	1,111 (13)	1,387 (14)
$[CH_3-4-C_6H_4CO]^+$ $[SbCl_6]^-$	1,097 (9)	1,396 (10)

L'ion méthyl-2-phényloxocarbonium peut être décrit par les formes mésomères suivantes :
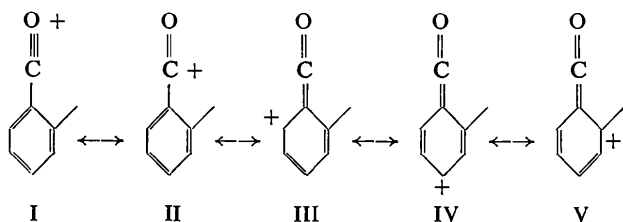
Si l'on examine les longueurs des liaisons dans le cycle benzénique, on constate que les valeurs les plus courtes correspondent aux liaisons C(4)–C(5) = 1,359 Å et C(6)–C(7) = 1,375 Å. Ce résultat exprime que la forme mésomère (V) où la charge positive est stabilisée par la présence du groupement méthyle contribue essentiellement à la structure de cet ion méthyl-2-phényloxocarbonium (Fig. 3). La même particularité est également présente dans la structure de l'ion méthyl-4-phényloxocarbonium (Chevrier, Le Carpentier & Weiss, 1972).

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The Crystal Structure of Potassium Hydrogen Bis(homophthalate), $K(C_9H_7O_4)_2.(H)$

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The crystal structure of potassium hydrogen bis(homophthalate), $K.(C_9H_7O_4)_2.(H)$, has been determined by X-ray diffraction and refined by the method of least squares to an R value of 0·099. The potassium ion lies on a twofold axis $(0, y, \frac{1}{4})$ in a monoclinic unit cell with $a=32·66_5$, $b=5·51_2$, $c=9·97_0$ Å, $\beta=95·9°$, $Z=4$ formula units of $K.(C_9H_7O_4)_2.(H)$; space group $C2/c$. There is fourfold coordination around the potassium ion with potassium–oxygen distances ranging from 2·76 to 2·80 Å. The molecules are held together by van der Waals contacts, metal–oxygen ionic linkages, a short hydrogen bond of 2·59 Å between oxygen atoms belonging to carboxyl groups of adjacent homophthalic acid units and an ultrashort symmetrical hydrogen bond of 2·41 Å between two centrosymmetrically related oxygen atoms with the proton on a centre of symmetry. The carboxyl groups are rotated out of the plane of the central aromatic ring by 18°58′ and 95°44′.

Introduction

The crystal structure of homophthalic acid (toluene-α-2-dicarboxylic acid, $C_9H_8O_4$) has been reported by Gupta & Sahu (1971). The potassium salt is of interest from the point of view of structural crystallography. Firstly, the composition of the compound can be written as $K.C_9H_8O_4.C_9H_7O_4$, as $K.(C_9H_{7·5}O_4)_2$, or

as $K(C_9H_7O_4)_2 \cdot (H)$, each formula representing a different structure. Secondly, some of the salts of dicarboxylic acids show unusual structures (Ferguson, Sime, Speakman & Young, 1968; Speakman, 1967; Srivastava & Speakman, 1961) and it was thought worthwhile to determine if the title compound exhibits similar features.

Crystal data

Crystals of potassium hydrogen bis(homophthalate) were grown from aqueous solution containing a trace of ethanol by mixing potassium hydroxide with homophthalic acid in stoichiometric amounts.

Crystals of $K \cdot (C_9H_7O_4)_2 \cdot (H)$ appear to be hexagonal thin plates with edges corresponding to the zone directions [010], [011] and [01$\bar{1}$], the angles [010]$\hat{\ }$[011] and [011]$\hat{\ }$[01$\bar{1}$] being 122°40′ and 118°30′ respectively. X-ray analysis of the crystals shows them to be monoclinic with $a = 32 \cdot 66_5$, $b = 5 \cdot 51_2$, $c = 9 \cdot 97_0$ Å, $\beta = 95 \cdot 9°$, $V = 1785 \cdot 6$ Å^3. The lattice parameters were determined from high $\sin\theta$ reflexions on Weissenberg films with silver lines superimposed as internal standards. The observed density is $1 \cdot 48_6$ g.cm^{-3}. This gives $1598 \cdot 4$ a.m.u for the total unit-cell content. The expected value for the empirical formula $\frac{1}{2}K \cdot (C_9H_{7 \cdot 5}O_4)$ ($Z = 8$) is 1592 a.m.u. Gravimetric analysis confirmed the absence of water of crystallization.

Space group absences:

$$hkl, \ h + k = 2n + 1$$

$$h0l, \ l = 2n + 1, \ (h = 2n + 1)$$

fix the space group as either $C2/c$ or Cc. $C2/c$ was preferred from intensity statistics, piezoelectric tests and the crystal morphology. The linear absorption coefficient for Cu $K\alpha$ radiation is $\mu = 30 \cdot 1$ cm^{-1}.

X-ray diffraction data were collected using a single crystal ($0 \cdot 03 \times 0 \cdot 02 \times 0 \cdot 01$ cm) and Weissenberg photography. 594 independent reflexions were collected; intensities were estimated visually and brought to a nearly absolute scale using statistical methods after the application of appropriate corrections. No correction for absorption was applied.

Structure determination and refinement

The structure was solved in a straightforward manner. As there are only four potassium ions present they must lie on special positions. Initially they were assigned the coordinates $0,\frac{1}{2},0$; $0,\frac{1}{2},\frac{1}{2}$. The [010] axis Fourier projection based on potassium dominated signs readily gave the positions of the light atoms in the molecule. The inclusion of the light-atom contributions reduced $R(h0l)$ to $0 \cdot 17$. A projection of a model of the molecule on the (001) plane gave acceptable values for the y coordinates, and $R(hk0)$ dropped to $0 \cdot 27$. However, at the stage of the refinement of the three-dimensional diffraction data, it was obvious that

the original choice of special positions for the potassium ions was wrong and the correct positions were on the diad axes $0,y,\frac{1}{4}$; $0,\bar{y},\frac{3}{4}$. With this change, the refinement soon converged by full-matrix least-squares refinement (using the program ORFLS of Busing, Martin & Levy, 1962, as modified by Hamilton, Ibers, Srikanta & Johnson for use on the CDC–3600 computer), with unit weights for all observed reflexions and anisotropic temperature factors for all non-hydrogen atoms, to the final $R(hkl)$ of $0 \cdot 099$. Hydrogen atoms were not included. The coordinates of the atoms are given in Table 1, a list of observed and calculated structure factors in Table 2, and the thermal parameters in Table 3.

Table 1. *Fractional coordinates with their e.s.d.'s* ($\times 10^4$)

	x/a	y/b	z/c
C(1)	1114 (4)	3972 (36)	3130 (16)
C(2)	1441 (4)	2863 (37)	2357 (14)
C(3)	1830 (4)	4012 (38)	2471 (15)
C(4)	2136 (4)	3090 (46)	1720 (17)
C(5)	2071 (4)	1007 (45)	967 (17)
C(6)	1696 (5)	−87 (40)	824 (15)
C(7)	1369 (4)	819 (40)	1624 (14)
C(8)	977 (4)	−733 (37)	1527 (15)
C(9)	609 (5)	392 (41)	626 (13)
O(1)	756 (3)	3527 (24)	2847 (11)
O(2)	1254 (3)	5455 (25)	4085 (11)
O(3)	279 (3)	−653 (30)	808 (10)
O(4)	652 (3)	1943 (25)	−201 (11)
K	0	5788 (14)	2500 (00)

Results

Bond lengths, valency angles and intermolecular distances

Fig. 1 gives the labelling of the atoms. The bond lengths are given in Table 4 and the angles in Table 5. Table 6 gives a list of intermolecular contacts less than 4·0 Å.
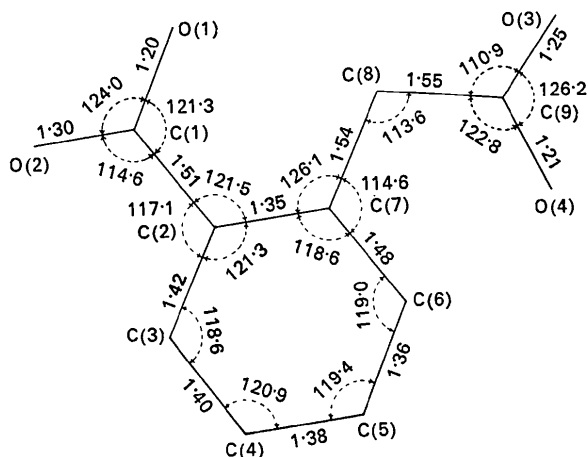

Fig. 1. Labelling scheme of the atoms.

Table 2. *Observed and calculated structure factors*

Table 3. *Thermal parameters* ($\times 10^5$) *with their e.s.d.'s*

The parameters are of the form:

$$T = \exp\left[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)\right].$$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	69 (16)	526 (951)	1009 (180)	126 (111)	88 (51)	253 (421)
C(2)	46 (13)	747 (810)	852 (166)	−150 (101)	−10 (44)	−316 (425)
C(3)	56 (13)	3686 (1138)	985 (169)	54 (131)	−37 (44)	557 (488)
C(4)	49 (14)	3621 (1133)	1373 (225)	62 (126)	62 (53)	50 (558)
C(5)	48 (14)	3404 (1243)	1467 (245)	97 (127)	5 (52)	272 (560)
C(6)	88 (16)	2367 (1013)	1116 (184)	181 (130)	103 (50)	413 (458)
C(7)	68 (14)	2014 (970)	710 (152)	13 (123)	1 (45)	363 (473)
C(8)	39 (11)	1562 (914)	1295 (191)	−57 (108)	−45 (42)	259 (452)
C(9)	98 (19)	1909 (1008)	460 (131)	−27 (129)	−60 (45)	972 (409)
O(1)	55 (10)	2492 (675)	1579 (155)	5 (75)	39 (33)	−421 (309)
O(2)	90 (10)	1640 (635)	1234 (137)	157 (82)	−75 (33)	−840 (324)
O(3)	70 (10)	6394 (922)	1229 (138)	−404 (96)	−28 (33)	1416 (383)
O(4)	62 (10)	2663 (675)	1428 (147)	−33 (79)	3 (35)	1102 (358)
K	58 (5)	3305 (375)	1782 (80)	0 (0)	54 (17)	0 (0)

Table 4. *Bond lengths with their e.s.d's*

C(1)–C(2)	1·507 (0·021) Å		C(7)–C(8)	1·541 (0·022) Å
C(2)–C(3)	1·416 (0·030)		C(8)–C(9)	1·553 (0·021)
C(3)–C(4)	1·404 (0·022)		C(1)–O(1)	1·201 (0·017)
C(4)–C(5)	1·376 (0·032)		C(1)–O(2)	1·301 (0·021)
C(5)–C(6)	1·360 (0·023)		C(9)–O(3)	1·251 (0·020)
C(6)–C(7)	1·483 (0·021)		C(9)–O(4)	1·205 (0·022)
C(7)–C(2)	1·350 (0·027)			

Planarity of the molecule

The least-squares plane passing through the central aromatic ring of atoms C(2) ~ C(7) is given by:

$$X - 2\cdot3638\,Y + 3\cdot2136Z - 8\cdot3216 = 0 \qquad (A).$$

The equation of the plane passing through the carboxyl group C(1)–O(1)–O(2) is:

$$X - 358\cdot80\,Y + 308\cdot40Z - 175\cdot60 = 0 \qquad (B).$$

The equation of the plane passing through the atoms of the second carboxyl group C(9)–O(3)–O(4) is:

$$X - 3\cdot0940\,Y - 3\cdot1669Z + 0\cdot5766 = 0 \qquad (C).$$

X, Y, Z are referred to the orthogonal axes a, b and c^*.

Planes (B) and (C) make angles of $18°\,58'$ and $95°\,44'$ respectively with the plane (A). The deviations of atoms from the plane (A) are given in Table 7. The direction cosines of the normals to the planes (A), (B) and (C) with respect to orthogonal axes a, b and c^* are given in Table 8.

Table 5. *Bond angles with their e.s.d's*

O(1)–C(1)–O(2)	124·0 (1·2)°		C(6)–C(7)–C(2)	118·6 (1·5)°
O(1)–C(1)–C(2)	121·3 (1·2)		C(7)–C(2)–C(3)	121·3 (1·4)
O(2)–C(1)–C(2)	114·6 (1·1)		C(6)–C(7)–C(8)	114·6 (1·3)
C(1)–C(2)–C(3)	117·1 (1·3)		C(2)–C(7)–C(8)	126·1 (1·3)
C(1)–C(2)–C(7)	121·5 (1·3)		C(7)–C(8)–C(9)	113·6 (1·3)
C(2)–C(3)–C(4)	118·6 (1·4)		C(8)–C(9)–O(3)	110·9 (1·2)
C(3)–C(4)–C(5)	120·9 (1·5)		C(8)–C(9)–O(4)	122·8 (1·3)
C(4)–C(5)–C(6)	119·4 (1·5)		O(3)–C(9)–O(4)	126·2 (1·3)
C(5)–C(6)–C(7)	119·0 (1·4)			

Table 6. *Intermolecular distances*

The primes denote the following symmetry transformations:

None	x, y, z;	"	$\bar{x}, y, \frac{1}{2}-z$;
'	$\bar{x}, \bar{y}, \bar{z}$;	'''	$x, \bar{y}, \frac{1}{2}+z$.

An atom designated as $_aC(1)$ indicates carbon atom C(1) translated by unit a translation *etc*. Atoms related by C centring are shown with an asterisk (*).

C(1)···C(6''')	3·79 Å	C(1)···C(8''')	3·89 Å
C(1)···C(9''')	3·94	C(1)···$_b$O(4''')	3·26
C(2)···C(6'')	3·79	C(3)···C(6''')	3·97
C(4)···C*(4'')	3·86	C(4)···$_b$C*(4'')	3·86
C(4)···C*(5'')	3·66	C(4)···C*(5')	3·94
C(5)···$_b$C*(3'')	3·92	C(5)···C*(5')	3·92
O(2)···C(6''')	3·65	O(2)···$_b$C(6''')	3·33
O(2)···$_b$C(7''')	3·25	O(2)···C(8''')	3·74
O(2)···$_b$C(8''')	3·96	O(2)···$_b$C(9''')	3·56
O(1)···O(4''')	3·62	O(1)···$_b$O(4''')	3·20
O(1)···O(3''')	3·82	O(1)···C(9''')	3·58
O(1)···C(8''')	3·97	O(3)···O(4')	3·12
O(2)···$_b$O(4''')	2·59	} H-bonds	
O(3)···O(3')	2·41		

Table 7. *Atomic deviations from the least-squares planes of the central aromatic ring*

	Deviation	e.s.d.'s	
C(1)	−0·049 Å	0·027 Å	
C(2)	−0·018	0·025	
C(3)	0·013	0·026	
C(4)	−0·016	0·031	
C(5)	0·028	0·031	Aromatic ring
C(6)	−0·031	0·028	
C(7)	0·023	0·027	
C(8)	0·134	0·026	

Table 8. *Direction cosines of the normals to the planes*

	l	m	n
Normal to plane (A)	0·2432	−0·5748	0·7814
Normal to plane (B)	0·0021	−0·7584	0·6518
Normal to plane (C)	0·2203	−0·6817	−0·6977

Coordination polyhedron around the potassium ion

The potassium ion is surrounded by four oxygen atoms belonging to four different molecules in a tetrahedral arrangement (Fig. 2). The potassium–oxygen distances are given in Table 9.

Table 9. *Metal–oxygen contact distances*

K···O(1)	2·76 Å
K···O(1'')	2·76
K···$_b$O(3)	2·80
K···$_b$O(3'')	2·80

Discussion of the structure

Figs. 3 and 4 show views of the crystal structure down [010] and [100] respectively. In the crystal, the linkages may be thought to be of the following types:

(i) metal–oxygen ionic linkages (2·76 to 2·80 Å),
(ii) a short hydrogen bond of 2·59 Å between adjacent molecules O(2)···$_b$O(4'''),
(iii) an ultrashort symmetrical hydrogen bond of 2·41 Å O(3)···O(3'),
(iv) weak van der Waals contacts of 3·12 Å and upwards.

The two homophthalic acid species linked with one potassium ion may be thought of as forming a simple chelate complex. This unit is linked to another and similar arrangement of two species by short hydrogen bonds of 2·59 Å between the oxygen atoms of carboxyl groups, and also a short symmetrical hydrogen bond of 2·41 Å (between oxygen atoms) to a second similar arrangement of two molecules. The linked arrangements are themselves related by the c glide. It may also be noted that these hydrogen bonds form an extended system in the crystal with zigzag links in vertical columns parallel to [001].

The chemical composition of the compound

As Table 6 shows, the two short intermolecular contacts between the oxygen atoms of the carboxyl groups of the molecules are 2·59 and 2·41 Å. Both of these must be regarded as true hydrogen bonds. In the case of the 2·59 Å hydrogen bond, the angle C(1)–O(2)–$_b$O(4''') is

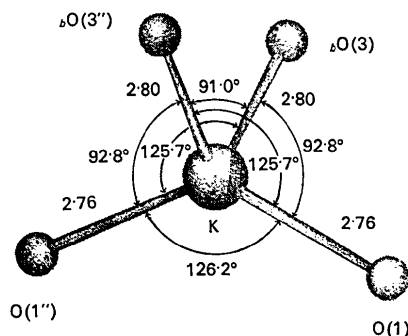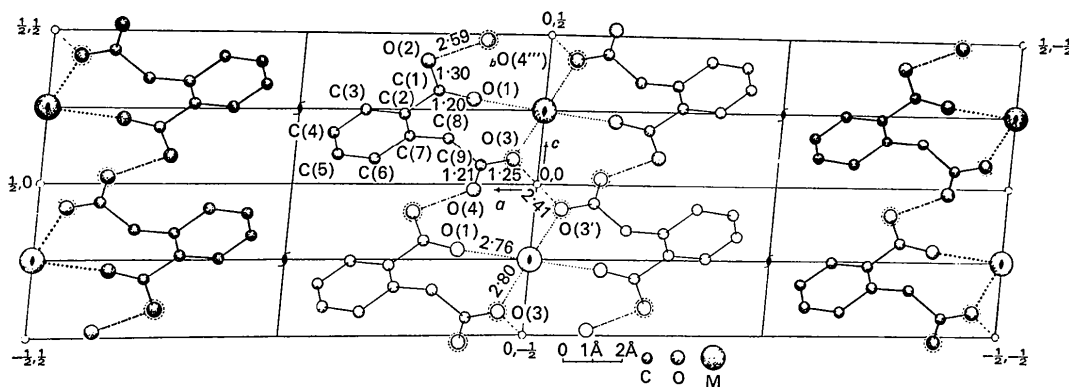
Fig. 2. Metal-oxygen polyhedra.
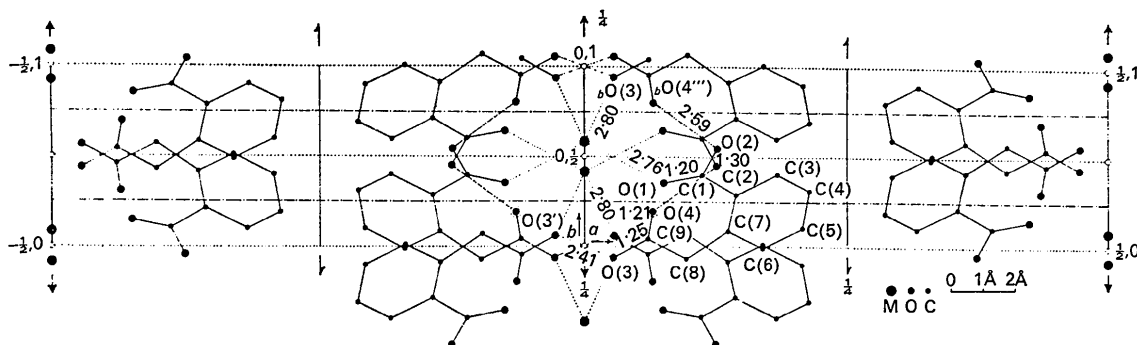
Fig.3. The crystal structure viewed down [010].

Fig.4. The crystal structure viewed down [100].

113°36', close to the expected tetrahedral value. Oxygen atom O(2) is the donor and $_b$O(4''') the acceptor. The angle C(9)–O(3)–O(3') is 111°54'. The hydrogen bond of 2·41 Å is a symmetrical hydrogen bond, with the proton on the special position 0,0,0, or oscillating midway between the oxygen atoms O(3) and O(3'). Such a symmetrical hydrogen bond has been reported (Ferguson et al., 1968) with nearly the same value (2·46 Å) for the bond length. Of the two carboxyl groups in homophthalic acid, one, O(1)–C(1)–O(2), is unionized, as evidenced by the significantly different ($>2\sigma$) C–O bond lengths (1·20, 1·30 Å). The other, O(3)–C(9)–O(4), is ionized. In the formula unit $K(C_9H_8O_4) \cdot (C_9H_7O_4)$, therefore, of the four carboxyl groups {2[O(1)–C(1)–O(2)]+2[O(3)–C(9)–O(4)]} three are unionized {2[O(1)–C(1)–O(2)]+[O(3)–C(9)–O(4)]} and one is ionized [O(3)–C(9)–O(4)]. The unionized carboxyl group O(3)–C(9)–O(4) provides, in alternating sequence, the proton which occupies the special position. Thus the correct composition of the compound may be regarded as $K(C_9H_7O_4)_2 \cdot H$, although the units $K(C_9H_7O_4)$ or $K(C_9H_8O_4) \cdot (C_9H_7O_4)$ do not have any independent existence. An alternative approach would be to consider, following Skinner, Stewart & Speakman (1954), that in the structure we have only homopthalate ions $(C_9H_7O_4)^-$, K^+ ions and

protons, the last being statistically disordered near 0,0,0, thereby simulating an effectively symmetrical hydrogen bond.

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