The Structure of Potassium Benzilate

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Abstract. $KC_{14}H_{11}O_3$, monoclinic, space group $P2_1/c$, $a = 13\cdot43$ (2), $b = 9\cdot20$ (1), $c = 10\cdot40$ (2) Å; $\beta = 111\cdot0$ (1)°; $D_m = 1\cdot67$, $D_x = 1\cdot64$ g cm^{-3}, $Z = 4$; μ(Cu $K\alpha$) = $38\cdot82$ cm^{-1}. The structure was solved by the heavy-atom Patterson and Fourier techniques and refined by least squares to a final R value of $0\cdot095$ for 1238 observed reflections. In this structure the phenyl rings are planar within the experimental errors. The strong K—O bonds ($2\cdot64$ to $2\cdot88$ Å) and the weak van der Waals bonds tie any one layer of potassium benzilate molecules to its neighbouring layers parallel to (100).

Introduction. The structure determination of potassium benzilate (hereinafter, KB) was carried out in order to study the stereochemistry of benzilic acid and related compounds. Benzilic acid is an important analytical agent and its interactions with several transition metals have been studied (Biswas & Ranade, 1967). The mechanism of benzilic acid rearrangement (Hine & Haworth, 1958), which has been studied in many cases, can be elucidated by knowing the details of the molecular structure. The use of benzilic acid in polymers, medicine and analytical chemistry suggests the important role played by it in different fields.

KB was prepared by neutralization of benzilic acid with potassium hydroxide. Single, needle-shaped crystals of suitable size were grown from aqueous solution. The systematic absences (*h0l* for $l = 2n + 1$, *0k0* for $k = 2n + 1$) uniquely determined the space group as $P2_1/c$. The X-ray diffraction data were collected by the photographic equi-inclination Weissenberg method using Cu $K\alpha$ radiation. The intensities of all 1238 reflections (from extended spots in higher layers) were estimated by the visual method with a suitable scale prepared. Intensities were corrected for the Lorentz–polarization factor as well as for the effect of spot extension (Phillips, 1954); absorption correction was neglected. Preliminary interlayer scaling was done with the help of *hk*0-type common reflections from the other axis using a similar crystal.

The structure has been solved by the heavy-atom method. The positional parameters of K ($0\cdot460, 0\cdot050, 0\cdot275$) only, obtained from a three-dimensional sharpened Patterson map, were used to calculate the first three-dimensional Fourier map, which gave the

positions of seven more atoms. Successive Fourier-map calculations revealed the complete structure with an R index of $0\cdot26$. Atomic coordinates, scale factors for individual layers and isotropic temperature factors were then refined by a full-matrix least-squares program (Busing, Martin & Levy, 1962) to an R index of $0\cdot15$. Further refinement with anisotropic thermal parameters was not effective and erratic results were obtained. Use of cross-reflections (Lingafelter & Donohue, 1966; Rae, 1965; Rae & Blake, 1966) for the

Table 1. *Fractional coordinates* ($\times 10^4$) *with their standard deviations in parentheses*

|	x	y	z
K	4646 (2)	317 (3)	2813 (3)
C(1)	6863 (7)	1410 (12)	1083 (11)
C(2)	7849 (8)	2252 (8)	1688 (13)
C(3)	8552 (9)	1785 (14)	2960 (16)
C(4)	9510 (9)	2557 (15)	3572 (18)
C(5)	9699 (10)	3813 (19)	2963 (21)
C(6)	8997 (11)	4306 (19)	1741 (19)
C(7)	8025 (8)	3530 (14)	1046 (15)
C(8)	7045 (8)	−41 (13)	418 (12)
C(9)	7675 (7)	−23 (11)	−363 (11)
C(10)	7824 (9)	−1392 (12)	−1011 (12)
C(11)	7326 (9)	−2669 (14)	−868 (15)
C(12)	6712 (10)	−2668 (13)	−73 (14)
C(13)	6554 (10)	−1337 (14)	540 (14)
C(14)	6058 (8)	2369 (11)	−19 (11)
O(1)	6490 (5)	1046 (7)	2138 (8)
O(2)	5723 (5)	3442 (9)	482 (9)
O(3)	5798 (5)	2112 (8)	−1268 (8)
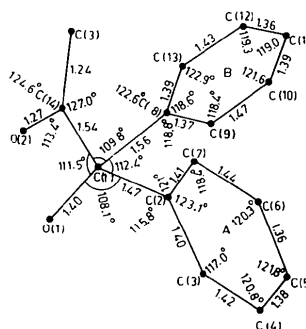
Fig. 1. Bond lengths (Å) and angles (°) for KB.

Table 2. *Equations of planes*

$lX + mY + nZ - p = 0$, where x,y,z are orthogonal coordinates (Å) referred to the crystallographic a, b and c^* axes.

	l	m	n	p
(1) Benzene ring A	0·6787	0·5486	0·4884	4·7639
(2) Benzene ring B	0·5364	0·2179	0·8154	1·8874
(3) Carboxylic group	0·8246	0·5642	0·0410	7·9476

Deviations of atoms from respective planes (Å $\times 10^4$)

Plane (1)

C(1)	108	C(2)	−219	C(3)	131	C(4)	−117
C(5)	71	C(6)	72	C(7)	−47		

Plane (2)

C(1)	116	C(8)	−158	C(9)	−40	C(10)	−20
C(11)	−163	C(12)	−119	C(13)	58		

Plane (3)

C(1)	−20	C(14)	85	O(2)	−29	O(3)	−34

proper scale factor enabled isotropic refinement to proceed to $R = 0.115$, and then further refinement with anisotropic thermal parameters gave the final R of 0·095. The three-dimensional difference Fourier map at this stage, however, could not reveal any definite H atom positions. The final positional parameters are given in Table 1.*

Discussion. The final bond lengths and bond angles are shown in Fig. 1; the estimated standard deviations (e.s.d.'s) in C—C and C—O bond lengths range between 0·01 and 0·03 Å, whereas in bond angles, the average e.s.d. is 1·5°. The least-squares plane through the two benzene rings and the carboxylic group have been calculated and are given in Table 2. The deviations of related atoms'from the respective planes indicate that the rings are planar within experimental error. In ring A bond lengths vary between 1·36 and 1·43 Å (average value, 1·40 Å) while in ring B they vary between 1·36 and 1·47 Å (average value, 1·40 Å). In both rings the central aromatic bonds are longer than the other aromatic bonds. All the angles in both the benzene rings are normal within experimental error. The dihedral angle between the two benzene ring planes is 85°.

The central carbon atom C(1) bonds tetrahedrally to O(1), C(2), C(8) and C(14) with bond lengths 1·40, 1·47, 1·56 and 1·54 Å respectively. The two C—O distances C(14)—O(3), 1·24, C(14)—O(2), 1·27 Å, suggest that the carboxylic acid group exists in a

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33241 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

disordered form (Leiserowitz, 1976). However, the possibility that the negative charge is entirely on one O atom cannot be ruled out. Fig. 2 shows the polyhedron formed by the neighbouring O atoms around the K ion,
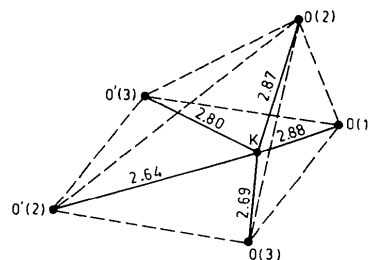

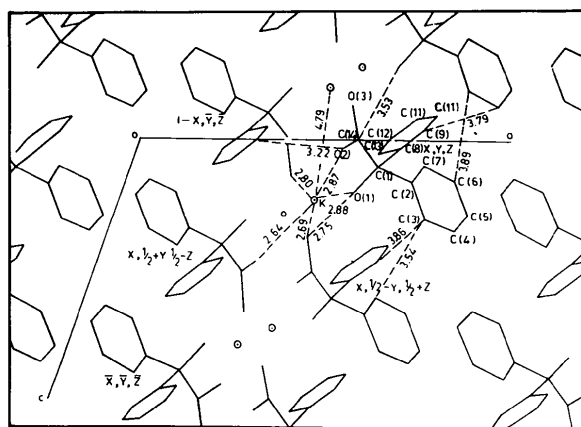Fig. 2. Environment of potassium, with bond lengths in Å.

Fig. 3. Structure projected on the (010) plane, with distances in Å.

Table 3. *Intermolecular distances* (Å)

S corresponds to equivalent positions: (1) x,y,z; (2) $\bar{x},\bar{y},\bar{z}$; (3) x, $\frac{1}{2}-y$, $\frac{1}{2}+z$; (4) $\bar{x}$, $\frac{1}{2}+y$, $\frac{1}{2}-z$. Ta, Tb, Tc denote translation along axes a, b, c, respectively.

Atom (x,y,z)	Atom $(S,TaTbTc)$		Atom (x,y,z)	Atom $(S,TaTbTc)$	
K	O(1) (1,000)	2·88	O(2)	C(12) (2,100)	3·22
K	O(2) (3,000)	2·87	O(2)	O(2) (2,110)	3·40
K	O(3) (2,100)	2·69	O(2)	O(3) (3,000)	3·38
K	O(2) (4,110)	2·64	O(3)	C(13) (2,100)	3·57
K	O(3) (3,000)	2·80	C(1)	O(3) (3,000)	3·78
K	K (2,101)	4·34	C(3)	C(7) (3,000)	3·54
K	K (4,100)	4·78	C(3)	C(9) (3,000)	3·86
K	K (4,110)	4·78	C(9)	C(6) (4,210)	3·68
K	C(9) (2,100)	3·25	C(5)	C(10) (4,200)	3·69
K	C(12) (4,100)	3·92	C(6)	C(10) (3,000)	3·78
K	C(12) (3,011)	3·75	C(9)	C(9) (3,001)	3·79
O(1)	C(7) (3,000)	3·86	C(9)	C(5) (4,210)	3·67
O(1)	C(11) (3,010)	3·68	C(6)	C(3) (3,001)	3·89
O(1)	O(2) (3,000)	3·99	C(11)	C(13) (3,011)	3·62
O(1)	O(3) (3,000)	2·75	C(14)	O(1) (3,011)	3·53

with K—O distances between 2·64 and 2·88 Å. In the crystal structure of the $\frac{2}{3}$ hydrate of potassium 5-ethyl-barbiturate (Gartland, Gatehouse & Craven, 1975) the range of seven K—O distances is 2·67 to 3·02 Å. In potassium glyconate monohydrate (Panagiotopoulos, Jeffery, La Placa & Hamilton, 1974) eight nearest-neighbour O atoms are in the range of distances 2·61 to 3·24 Å.

The projection of the crystal structure along **b** is shown in Fig. 3. The short K—O distances, K—K contacts and other significant distances are given in Table 3. The molecules, stacked in layers parallel to (100), are linked to each other through strong K—O and weak van der Waals bonds.

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(L-Phenylalaninato)dimethylthallium(III)

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Abstract. $C_{11}H_{16}NO_2Tl$, $M_r = 398·3$, triclinic, $P1$, $a = 11·278$ (2), $b = 9·354$ (3), $c = 6·231$ (2) Å, $\alpha = 105·53$ (4), $\beta = 78·75$ (3), $\gamma = 103·66$ (2)°, $U = 609·3$ Å^3, $Z = 2$, $D_c = 2·17$ g cm^{-3}, μ(Mo $K\alpha$) = 127 cm^{-1}, $F(000) = 372$. The complex, $(CH_3)_2Tl$(L-PHE), in the crystal consists of two independent polymeric chains of $(CH_3)_2Tl$(L-phenylalanine) units linked by the carboxyl groups [Tl—C = 2·06 (2), 2·15 (2); Tl—O = 2·65 (1), 2·63 (1); Tl—N = 2·53 (1) and Tl^i—C = 2·17 (2), 2·09 (2); Tl^i—O = 2·66 (1), 2·54 (1); Tl^i—N = 2·53 (1) Å]. Each independent Tl atom is approximately octahedrally coordinated with the sixth coordination site in each case occupied by a bridging carboxyl O atom of an adjacent polymeric chain [Tl—O = 3·13, 3·06 Å].

Introduction. Small, colourless irregular needles were obtained by crystallization from water. Unit-cell and intensity data were measured on a Philips PW 1100 automatic four-circle diffractometer with Mo $K\alpha$ radiation, a graphite monochromator and the θ–2θ

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scan technique (Henrick, Matthews & Tasker, 1978). Complete data sets were recorded for two crystals with $3 \leq \theta \leq 30°$. Both crystals were ca $0·07 \times 0·25 \times 0·15$ mm. There were no easily identifiable faces. For each data set the intensities of three standard reflections measured every 3 h decreased by ca 30% during data collection and were used to scale the data in each set to a common level. The data were corrected for Lorentz and polarization effects but not for absorption or extinction. The data sets consisted of 2443 and 3122 independent reflections respectively and were merged through common reflections by linear least squares (Rae & Blake, 1966) to give 3204 unique reflections (interlayer scale factors of 1·0011 and 0·9989 respectively), of which 18 with $I \leq 3\sigma(I)$ were considered to be unobserved. The Patterson function and an initial difference map were solved in the space group $P1$ and gave all the non-hydrogen atom positions but with a second phenyl ring ghosted above a complete $(CH_3)_2Tl$(L-PHE) molecule. The structure was refined from the centrosymmetrically related metal–ligand positions and the noncentrosymmetrically related