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The Crystal Structure of Potassium Acid Phthalate, $KC_6H_4COOH.COO$

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Crystals of potassium acid phthalate belong to the orthorhombic system with $a=6{\cdot}46_6$, $b=9{\cdot}60_9$, $c=13{\cdot}85_7$ Å; the space group is $P2_1ab$. The structure was studied by using three-dimensional data collected on a computer-controlled diffractometer operated by an IBM 1620 machine under a stored data-collection program.

The ionic structure consists of potassium ions and infinite chains of acid phthalate ions formed by short O–H · · · O hydrogen bonds through the a glide perpendicular to the b axis. The benzene ring is a slightly distorted regular hexagon and the two carboxyl groups are planar within experimental errors; a change in the shape of carboxyl groups with respect to the state of ionization is demonstrated in the structure. The un-ionized carboxyl group makes an angle of 31·7° with the benzene ring; the corresponding angle for the ionized one is 75·4°.

Introduction

The crystal structure of potassium acid phthalate was studied as a part of our study on *ortho*-substituted benzoic acids and their derivatives. The main purpose of this study is to obtain accurate information about the effect of steric hindrance of the two carboxyl groups on the over-all conformation of the phthalate ion. It is also of significance to compare the shapes of these two carboxyl groups, one being ionized and the other still possessing a proton.

Potassium acid phthalate belongs to a series of alkali acid phthalates which crystallize in the orthorhombic system and are listed by Groth (1917). The structure of the ammonium salt was reported several years ago (Okaya & Pepinsky, 1957). Although the latter structure is still to be refined, a comparison can be made between the two structures with respect to the general mode of packing of aromatic rings and also the coordination around the cations.

Experimental

A single crystal of potassium acid phthalate was ground into an approximately spherical shape and mounted on a General Electric goniostat which was placed on a Picker biplane diffractometer; the latter belongs to CCXD, a computer-controlled diffractometer (Cole, Okaya & Chambers, 1963), which is operated by an IBM 1620 machine under a stored data collection program. The unit-cell dimensions determined on the diffractometer and used as input parameters for the data collection programs are $a=6{\cdot}46_6$, $b=9{\cdot}60_9$, $c=13{\cdot}85_7$ Å. The crystal belongs to the orthorhombic class with space group $P2_1ab$.* There are four chemical units of the formula $K(C_6H_4\,.\,COOH\,.\,COO)$ in a unit cell. Three-dimensional integrated intensity was obtained from the specimen by using filtered Mo $K\alpha$ radiation. For each reflection, the alignment of the crystal and the accuracy of the instrument were first checked by optimizing the ω setting; the integrated intensity was then recorded by step-scanning around the 2θ axis. All non-equivalent reflections (1490) within the region of $\sin\theta/\lambda \le 0{\cdot}81$ with Mo $K\alpha$ radiation were recorded in such a manner. The detailed computer program for data collection is explained elsewhere (Okaya, 1964).

The crystal structure of potassium acid phthalate was determined and refined in a straightforward fashion by using the three-dimensional data thus obtained. The position of the potassium ion was obtained from a sharpened three-dimensional Patterson function and the usual heavy atom method of structure determination by electron-density calculation was used to obtain the other light atom positions. The structure was then refined by using a full-matrix least-squares program on an IBM 7094 computer (Okaya, 1963); the positions of hydrogen atoms were determined in the course of the refinement by the usual (F_o-F_c) synthesis method and also refined with isotropic temperature factors. The final conventional error factor $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ (excluding about a dozen unobserved reflections) was reduced to 0·044. The shifts in parameters in the final cycle are about 10^{-2} of the e.s.d.'s of the corresponding parameters. The weighting scheme used was as follows: $w=1{\cdot}0$ for $F_{\text{obs}}<20{\cdot}0$, $w=20{\cdot}0/F_{\text{obs}}$ for $F_{\text{obs}}\ge 20{\cdot}0$, and unobserved reflections were given zero weight. The atomic scattering factors used in the calculations were taken from *International Tables for X-ray Crystallography* (1962). The atomic coordinates, their standard deviations and thermal parameters at this stage are listed in Table 1. Comparison between the observed and calculated structure factors is given in Appendix I.*

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* The space group of this compound was given previously (Okaya & Pepinsky, 1957) as $P2_12_12$. The assignment depended on very weak (odd, 0, l) and (h, odd, 0) reflections. Since the structure was determined by the present space group to a high degree of precision, these reflections may be considered as accidental ones such as double reflections.

* Appendix I has been submitted with the manuscript and deposited as Document No. 8400 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C. A copy may be secured by citing the Document number and by remitting $ 5·00 for photoprints, or $ 2·25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Discussion

The crystal structure of potassium acid phthalate is, as expected, ionic consisting of potassium ions and acid phthalate ions; a short hydrogen bond of 2·546 Å is found between O(I) of the un-ionized carboxyl group of one phthalate ion to O(II′) of another ion related to the first by the *a* glide perpendicular to the *b* axis.* The potassium ion is surrounded by six oxygen atoms: three from O(II) with distances $2{\cdot}62_9$, $2{\cdot}77_4$ and $2{\cdot}98_6$ Å, two from O(II′) with $2{\cdot}78_7$ and $2{\cdot}80_3$ Å and finally one from O(I′) with $2{\cdot}86_3$ Å. It is quite obvious that O(I) which retains its proton is not coordinated to a potassium ion and also O(II′) which receives a hydrogen bond from O(I) is involved in only two K^+–O contacts. These K^+–O distances and the mode of coordination around the potassium ion are quite normal as compared to other potassium salts. In Fig. 1, a schematic drawing of the structure viewed along the *a* axis is shown. The acid phthalate ions make infinite chains along the *a* axis and the chains are connected with each other by polar or ionic parts of the structure formed by potassium ions near the plane $z=0$. The sheet-like layers perpendicular to the *c* axis thus formed stack in the structure through the non-polar parts along the *plane* $z=\frac{1}{2}$. The perfect cleavage perpendicular to the *c* axis is accounted for by such a structure. This is characteristic of the structures of salts of aromatic acids with predominant cleavage planes; *e.g.* the acid phthalates, the acid *o*-sulfobenzoates (Okaya, 1965) and others.

Table 1. (*a*) *Atomic coordinates in fractions of cell edges and their standard deviations in* 10^{-4} Å

K	0·25000	7	0·09898	7	0·03878	7
Carboxyl I						
C(I)	0·00561	30	−0·17780	33	0·21761	31
O(I)	0·07871	23	−0·29831	23	0·26258	25
O(I′)	0·01748	23	−0·16109	27	0·12732	24
Carboxyl II						
C(II)	−0·23842	27	0·06887	25	0·15685	27
O(II)	−0·15861	23	0·14522	24	0·09314	24
O(II′)	−0·40385	22	0·00006	24	0·14401	23
Benzene ring						
C(1)	−0·02519	28	−0·05921	30	0·28937	29
C(2)	0·06263	33	−0·06367	38	0·38466	34
C(3)	0·03824	32	0·04731	44	0·45050	33
C(4)	−0·07350	34	0·16280	40	0·42058	35
C(5)	−0·15805	33	0·16928	33	0·32513	34
C(6)	−0·13588	27	0·05799	29	0·25841	29
Hydrogen atoms						
H(O)	0·038		−0·380		0·235	
H(2)	0·140		−0·146		0·400	
H(3)	0·096		0·048		0·521	
H(4)	−0·091		0·237		0·464	
H(5)	−0·231		0·252		0·304	

(*b*) *Thermal parameters*

The β's are used in the usual expression for the effect of thermal vibration:

$$\exp\{-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})\}.$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	0·012933	0·007996	0·004356	−0·000936	0·000451	−0·004183
C(I)	0·011939	0·007362	0·003357	0·004251	−0·001477	−0·000377
O(I)	0·020479	0·005880	0·004036	0·005391	0·002362	0·000972
O(I′)	0·024750	0·008423	0·003208	0·007443	−0·000346	−0·000449
C(II)	0·010741	0·004613	0·003359	0·002603	−0·000418	−0·000018
O(II)	0·018351	0·007203	0·003951	−0·000170	0·001674	0·002903
O(II′)	0·012018	0·007009	0·003929	−0·002799	−0·002505	0·001101
C(1)	0·010635	0·005741	0·003046	0·000957	0·000451	0·000685
C(2)	0·016047	0·008974	0·003216	0·001590	−0·001639	0·000666
C(3)	0·016465	0·011221	0·003415	−0·002345	−0·001348	−0·002147
C(4)	0·014791	0·009739	0·004016	−0·002971	0·001962	−0·004054
C(5)	0·013529	0·006384	0·004389	0·000157	0·001684	−0·001914
C(6)	0·009404	0·005821	0·002960	−0·000725	0·000500	0·000056

(*c*) Isotropic temperature factors of hydrogen atoms in 10^{-16} cm^2

H(O)	H(2)	H(3)	H(4)	H(5)
4·8	2·2	5·0	1·6	2·4

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* Similar O–H · · · O bonds between acid phthalate ions in the ammonium salt were unfortunately overlooked in the previous paper (Okaya & Pepinsky, 1957). A complete rework on the ammonium salt structure is now being contemplated.

Bond angles and bond distances in the acid phthalate ion were calculated by using the atomic coordinates listed in Table 1. They are shown in Figs. 2 and 3. As is expected from the chemical formula of the compound, there are two carboxyl groups, one with its proton and the other which is ionized. The former un-

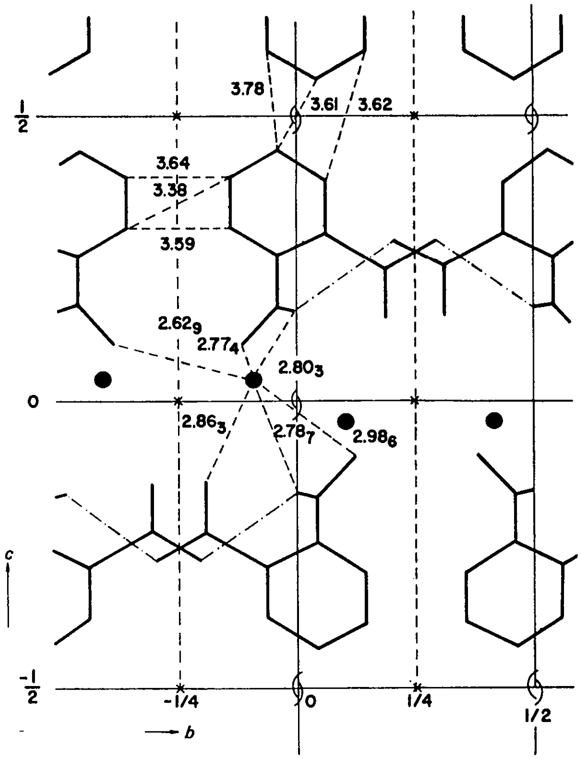

Fig. 1. A schematic drawing of the structure viewed along the *a* axis. The short O–H..O hydrogen bonds are shown by chain lines.

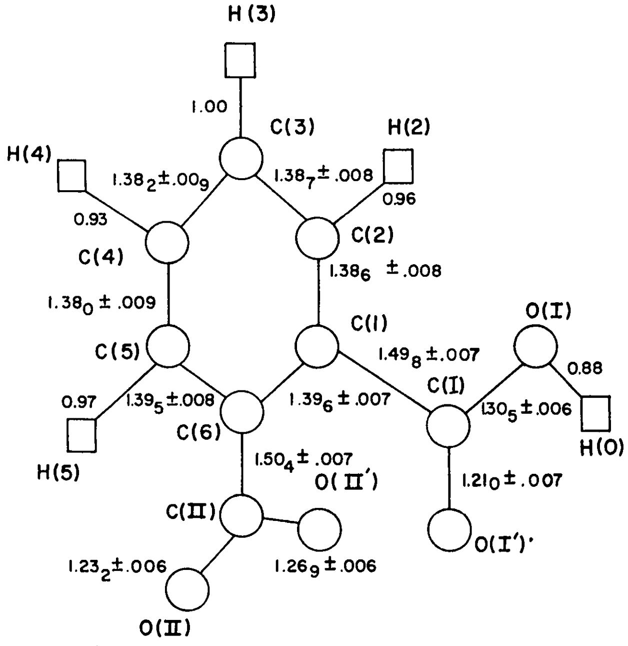

Fig. 2. Bond distances in the acid phthalate ion.

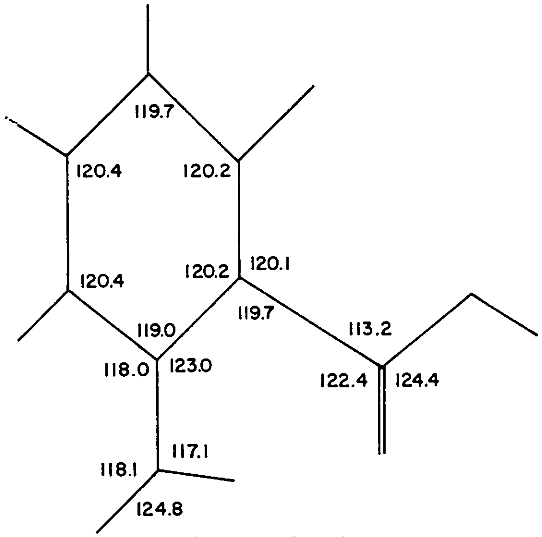

Fig. 3. Bond angles.

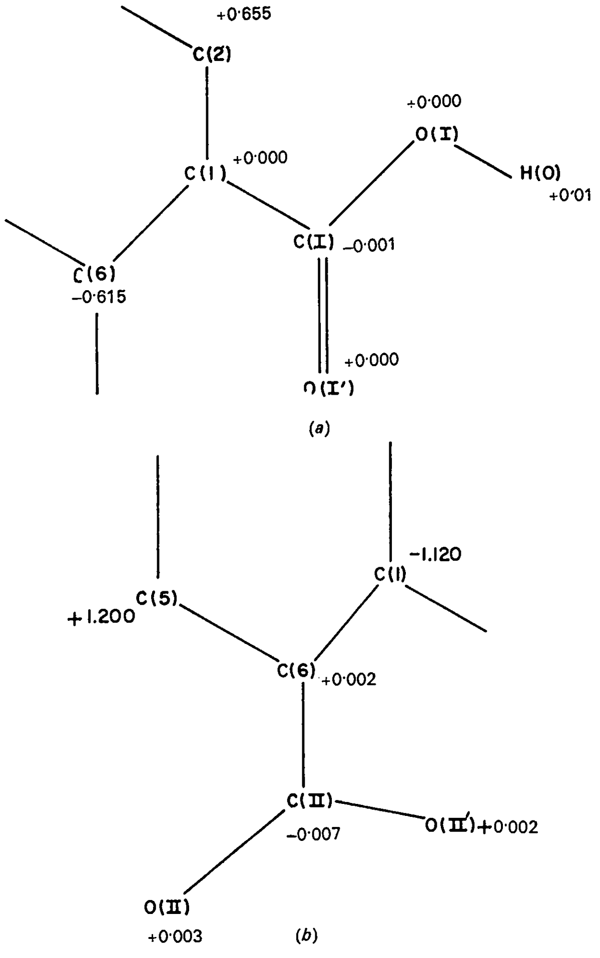

Fig. 4. (*a*) Deviations of atoms from the plane of carboxyl (I). C(2) and C(6) were excluded from the evaluation of the least-squares plane: $0\cdot9909\,X+0\cdot1105\,Y+0\cdot0769\,Z=0\cdot0966$. X, Y and Z are measured in Å. (*b*) Deviations of atoms from the plane of carboxyl (II); $-0\cdot5395\,X+0\cdot7738\,Y+0\cdot3319\,Z=2\cdot0261$. The deviations of C(5) and C(1) are also shown.

ionized carboxyl group has two distinct C–O distances: $1{\cdot}21_0$ for C=O and $1{\cdot}30_5$ Å for C–OH; as common to such a carboxyl group (*e.g.* see refined data on D-tartaric acid, Okaya & Stemple, 1965) there are again two C–C–O angles: narrow C–C–OH of 113·2° and wide C–C=O of 122·4°. In contrast to the situation in this carboxyl group, the ionized carboxyl (II) has two similar C–O distances and almost equivalent C–C–O angles. A similar story is found in the structure of potassium tetraoxalate, $K(C_2O_4H)\cdot(C_2O_4H_2)\,.\,2H_2O$, where one can find both ionized and un-ionized carboxyl groups (Haas, 1964). Regardless of the state of ionization and the difference in bond distances and angles, both C(1) – C(I) and C(6) – C(II) are equivalent and these two carboxyl groups are planar within experimental errors; for carboxyl (I), the hydrogen atom on O(I) is also in the plane of the group. The equations of these planes and the deviations of atoms from them are shown in Fig. 4.

The benzene ring is a slightly disorted regular hexagon with the average C–C distance of $1{\cdot}38_8$ Å and the C–C–C angle of 120°. All six bond distances and bond angles are within standard deviations from these average values. The equation of the ring plane is calculated in the usual manner and the deviations of atoms from the plane are shown in Fig. 5.

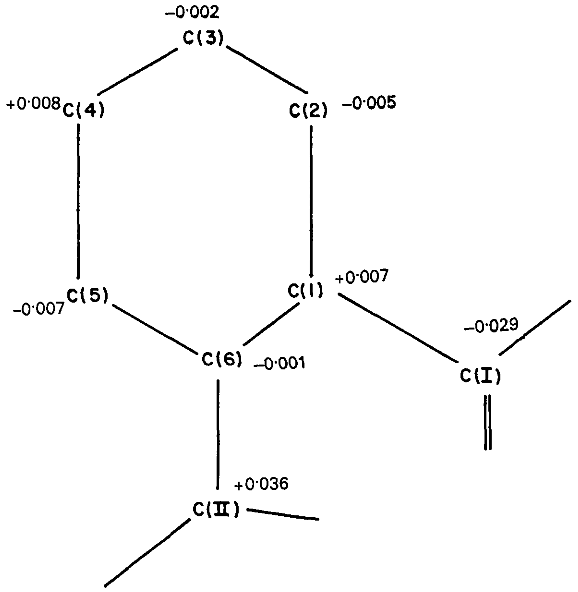

Fig. 5. Deviations of atoms from the benzene ring plane. The least-squares plane equation is: $-0{\cdot}8399\,X-0{\cdot}4111\,Y+0{\cdot}3543\,Z=1{\cdot}7008$.

Owing to steric hindrance caused by the two carboxyl groups in *ortho* positions, these carboxyl groups can no longer stay in the plane of the benzene ring. The angles between the ring plane and the carboxyl planes are 31·7° and 75·4° for groups (I) and (II), respectively. A similar situation can also be found in the structure of dipotassium ethylenetetracarboxylate, $K_2(COOH-COO\,.\,C=C-COO\,.\,COOH)$ (Kumra & Darlow, 1965). The angle between the central part of this centrosymmetric ion and the un-ionized carboxyl group is 34·1°; the corresponding angle for the ionized one is 77·4°.* These angles are to be compared with those made by the two equivalent carboxyl groups (33°) found in phthalic acid (Nowacki & Jaggi, 1957). The effect of steric hindrance can also be seen in the deviations of C(I) and C(II) from the benzene ring, C(I) by $-0{\cdot}22_9$ Å and C(II) by $+0{\cdot}03_6$ Å. Since the two carboxyl groups are quite planar, these deviations of C(I) and C(II) correspond to the twist of these two groups in opposite directions. The steric hindrance also affects the angles around C(6) to give a larger separation between the carboxyl groups.

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References

COLE, H., OKAYA, Y. & CHAMBERS, F. W. (1963). *Rev. Sci. Instrum.* **34**, 872.

GROTH, P. (1917). *Chemische Krystallographie*, Vol. 4, p. 724. Leipzig: Engelmann.

HAAS, D. J. (1964). *Acta Cryst.* **17**, 1511.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

KUMRA, S. K. & DARLOW, S. F. (1965). *Acta Cryst.* **18**, 98.

NOWACKI, W. & JAGGI, H. (1957). *Z. Kristallogr.* **109**, 272.

OKAYA, Y. (1963). Abstract, ACA Computer Conference, IBM Research Center.

OKAYA, Y. (1964). Unpublished.

OKAYA, Y. (1965). To be published.

OKAYA, Y. & PEPINSKY, R. (1957). *Acta Cryst.* **10**, 324.

OKAYA, Y. & STEMPLE, N. R. (1965). *Acta Cryst.* Submitted for publication.

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* Since the positions of the protons have not been established unambiguously in their structure, the authors did not make the assignment of the carboxyl groups. However, judging by the bond lengths and angles in these carboxyl groups and also by the hydrogen-bond scheme in the crystal, it is relatively easy to decide which of the two groups in the asymmetric unit retains its proton (H on the oxygen atom listed as O(3) in their paper).