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TOPOCHEMICAL STUDIES. I. THE CRYSTAL AND MOLECULAR STRUCTURE OF POTASSIUM DIHYDROGEN *trans*-ACONITATE, $K^+(HOOC.CH_2.C(COOH)=CH.COO)^-$

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Crystals of potassium dihydrogen *trans*-aconitate, $C_6H_5O_6K$, are monoclinic, *a*=11.856, *b*=15.920, *c*=8.426 Å, β=90.88°, *Z*=8, and space group *C*2/*c*. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares method to *R*=0.060 for 1677 independent non-zero reflections measured by four-circle diffractometry. There are two types of hydrogen bonds; one is intramolecular (2.53 Å) and the other is intermolecular (2.52 Å). The distances between neighboring double-bonds are longer than 4.96 Å; hence the molecules are too far away to dimerize by ultraviolet light.

Photochemistry of unsaturated carboxylic acids has become of interest in recent years. For example, *trans*, *trans*-muconic acid, whose structure has been determined by one of the authors,1) gives vinyl-substituted cyclobutanes and various oligomers on irradiation with ultraviolet light.2) This phenomenon has been explained by Schmidt and his collaborators as "topochemical" effect.3) In this connection, we have determined the molecular conformation and crystal structure of potassium dihydrogen *trans*-aconitate by a three-dimensional X-ray analysis.

Crystals of potassium dihydrogen *trans*-aconitate were prepared from aqueous solution by slow evaporation. The crystals were yellow prisms elongated along *c*-axis.

Crystal data: Formula weight=212.2, monoclinic, *a*=11.856(2), *b*=15.920(3), *c*=8.426(2) Å, β=90.88(3)°, *V*=1590.2 A^3, *Z*=8, *Dm*=1.769(by flotation), *Dc*=1.773 $g.cm^{-3}$, μ=6.6 cm^{-1} for Mo *K*α. *F*(000)=864.

Systematically absent spectra: *hkl* when *h*+*k* odd, *h*0*l* when *h* odd and *l* odd, 0*k*0 when *k* odd. Possible space group is *Cc* or *C*2/*c*. Structure analysis was made on the basis of the latter space group symmetry and gave a reasonable structure.

Lattice constants and intensities were measured from a crystal of dimensions *ca*. 0.2 x 0.1 x 0.1 mm, on a Rigaku automatic four-circle diffractometer with Zr-filtered Mo *K*α radiation using scintillation counter with pulse-height analyser. The ω-2θ scan technique was employed with scan speed 2°/min in 2θ. Background was measured for 15 sec on either side of the peak. A total of 1824 independent reflections were surveyed in the range, $0<\sin\theta/\lambda<0.65$. The corrections for Lorentz and polarization factors were made, but no corrections for absorption were applied.

In the course of measurement, it was recognized that peak profile became broad and integrated intensity declined. The correction for this was made at the stage of refinement; the data were grouped according to the exposure time and each group of them was re-scaled using an average ratio of |*Fo*| and |*Fc*| in the group.

The positions of two kinds of potassium ions (on two-fold axis) were obtained from a three-dimensional Patterson map. Twelve remaining non-hydrogen atoms were found from a three-dimensional Fourier map synthesized with the potassium signs. Refinement was made by block-diagonal least-squares calculations with anisotropic temperature factors. Five hydrogen atoms were obtained from a difference synthesis. Further refinement including the hydrogen atoms with isotropic temperature factors reduced *R* to 0.060 for 1677 non-zero reflections. The atomic scattering factors were taken from International Tables for X-ray Crystallography.[4)] All computations were performed on a HITAC 5020E computer at the Computer Center of the University of Tokyo using the UNICS program system.[5)]

The final fractional co-ordinates and thermal parameters are listed in Table 1. The crystal structure viewed along the *b*-axis is shown in Fig. 1. The bond lengths and angles are shown in Fig. 2.

The O-H...O intermolecular hydrogen bonds link aconitate ions along [101] infinitely to form chains, and the O(6)-H(5)...O(2) intramolecular hydrogen bond forms eight membered ring. Each of the two kinds of potassium ions is co-ordinated closely

Table 1. Fractional atomic co-ordinates and thermal parameters with significant figures of e.s.d's in parentheses
Anisotropic temperature factors are expressed as

$$\exp(-\underline{b}_{11}\underline{h}^2 - \underline{b}_{22}\underline{k}^2 - \underline{b}_{33}\underline{l}^2 - \underline{b}_{12}\underline{hk} - \underline{b}_{13}\underline{hl} - \underline{b}_{23}\underline{kl}),$$

and all values of $\underline{b}_{ij}$ should be multiplied by 10^{-4}. Isotropic temperature factors are of the form: $\exp(-\underline{B}\sin^2\theta/\lambda^2)$ with $\underline{B}$ values in $\mathring{A}^2$.

	x	*y*	*z*	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
K(1)	0.00000(0)	0.07398(6)	0.75000(0)	43(1)	15(0)	104(1)	0(0)	8(1)	0(0)
K(2)	0.50000(0)	0.13807(6)	0.75000(0)	87(1)	17(0)	87(1)	0(0)	-23(2)	0(0)
C(1)	0.2916(2)	0.2057(2)	0.2703(3)	38(2)	22(1)	70(4)	-6(2)	-20(4)	11(3)
C(2)	0.2161(2)	0.1439(2)	0.2723(3)	32(2)	18(1)	50(3)	3(2)	6(4)	5(3)
C(3)	0.2122(2)	0.0719(2)	0.3891(3)	36(2)	18(1)	64(4)	1(2)	7(4)	4(3)
C(4)	0.3915(2)	0.2133(2)	0.3803(3)	32(2)	23(1)	72(4)	-12(2)	-7(4)	5(3)
C(5)	0.1233(2)	0.1430(2)	0.1479(3)	31(2)	19(1)	57(3)	-1(2)	5(4)	3(3)
C(6)	0.2788(2)	-0.0045(2)	0.3346(3)	46(2)	20(1)	79(4)	5(2)	-8(5)	-1(3)
O(1)	0.4266(2)	0.2866(1)	0.4071(3)	49(2)	23(1)	120(4)	-20(2)	-65(4)	19(3)
O(2)	0.4351(2)	0.1493(1)	0.4425(3)	53(2)	24(1)	136(4)	-2(2)	-76(4)	4(3)
O(3)	0.0800(2)	0.0775(1)	0.1051(2)	46(2)	22(1)	90(3)	-11(2)	-28(3)	-3(3)
O(4)	0.0945(2)	0.2170(1)	0.0933(3)	56(2)	20(1)	125(4)	4(2)	-88(4)	2(3)
O(5)	0.2367(2)	-0.0703(1)	0.2961(3)	68(2)	19(1)	120(4)	-2(2)	-8(4)	-21(3)
O(6)	0.3886(2)	0.0050(2)	0.3334(4)	40(2)	27(1)	276(6)	12(2)	4(5)	-52(4)
H(1)	0.287(3)	0.249(2)	0.189(4)	1.0(8)					
H(2)	0.133(3)	0.051(2)	0.399(4)	0.3(7)					
H(3)	0.244(3)	0.089(2)	0.491(4)	1.1(8)					
H(4)	0.026(4)	0.212(3)	0.023(5)	2.5(10)					
H(5)	0.411(4)	0.055(3)	0.369(6)	4.3(13)					

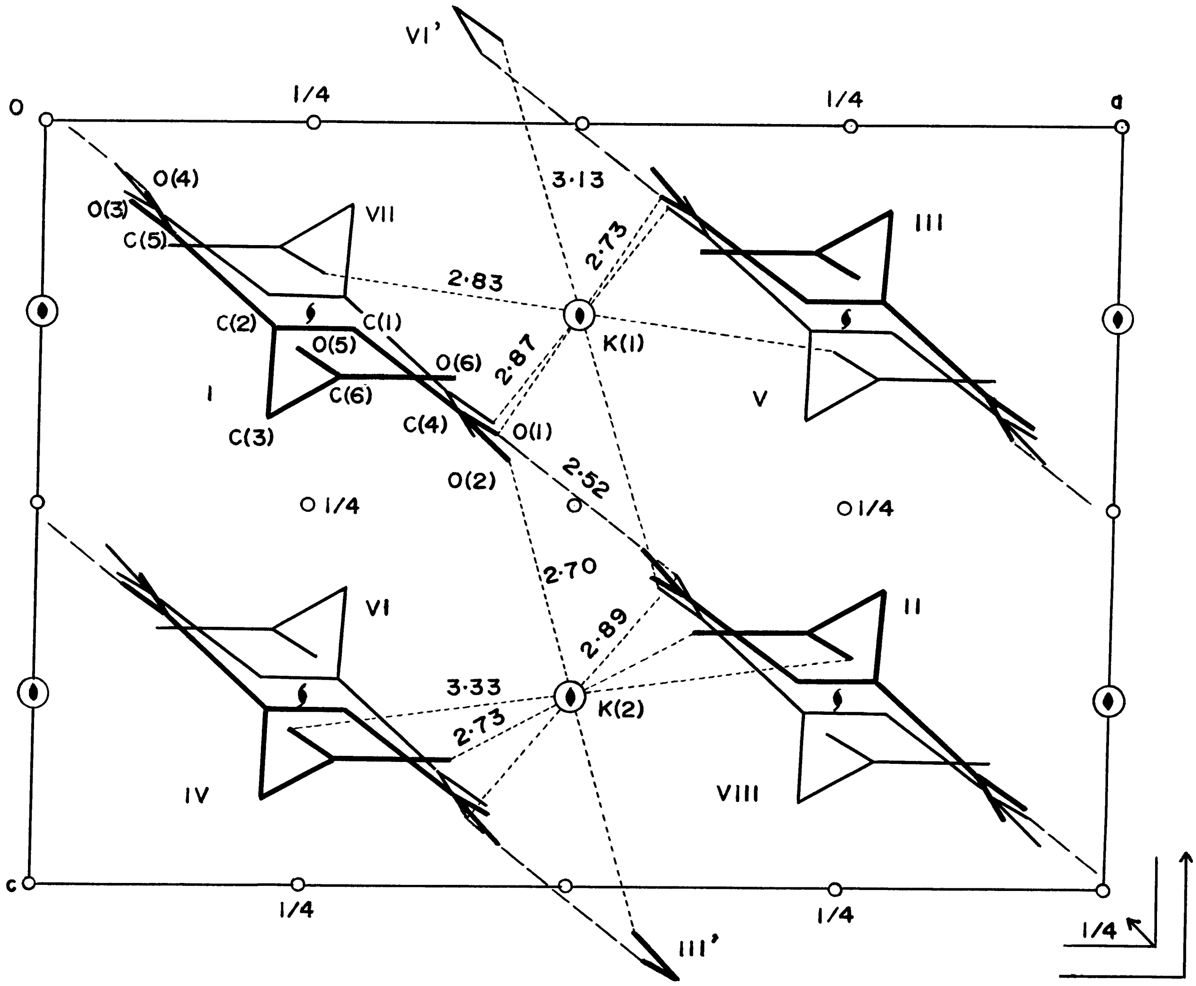

Fig. 1. Crystal structure viewed along the *b*-axis.
Intermolecular hydrogen bonds are shown by broken lines, and co-ordinations of the oxygen atoms to each of the two kinds of potassium ions by dotted lines.

Key for molecules I: *x*, *y*, *z* II: 1-*x*, -*y*, 1-*z* III: 1-*x*, *y*, 1/2-*z*
III': 1-*x*, *y*, 3/2-*z* IV: *x*, -*y*, 1/2+*z* V: 1/2+*x*, 1/2+*y*, *z*
VI: 1/2-*x*, 1/2-*y*, 1-*z* VI': 1/2-*x*, 1/2-*y*, -*z*
VII: 1/2-*x*, 1/2+*y*, 1/2-*z* VIII: 1/2+*x*, 1/2-*y*, 1/2+*z*

by six oxygen atoms and loosely by two oxygen atoms; moreover each of six oxygen atoms of aconitate ion is co-ordinated closely by one of the potassium ions.

The O(1)-C(4)-O(2) carboxyl group seems to be ionized because two C-O bond lengths are indistinguishable. In the other two carboxyl groups, the bond lengths are normal for unionized one. The C(1), C(2), C(3), C(4) and C(5) atoms are approximately on a least-squares plane. The O(1)-C(4)-O(2) and O(3)-C(5)-O(4) carboxyl groups, which are approximately parallel to each other, are twisted from this plane by 29.3° and 28.6° respectively, and the O(5)-C(6)-O(6) carboxyl group by 68.4°. Since the distances between carbon-carbon double bonds are longer than 4.96 Å, the crystals may be light-stable.

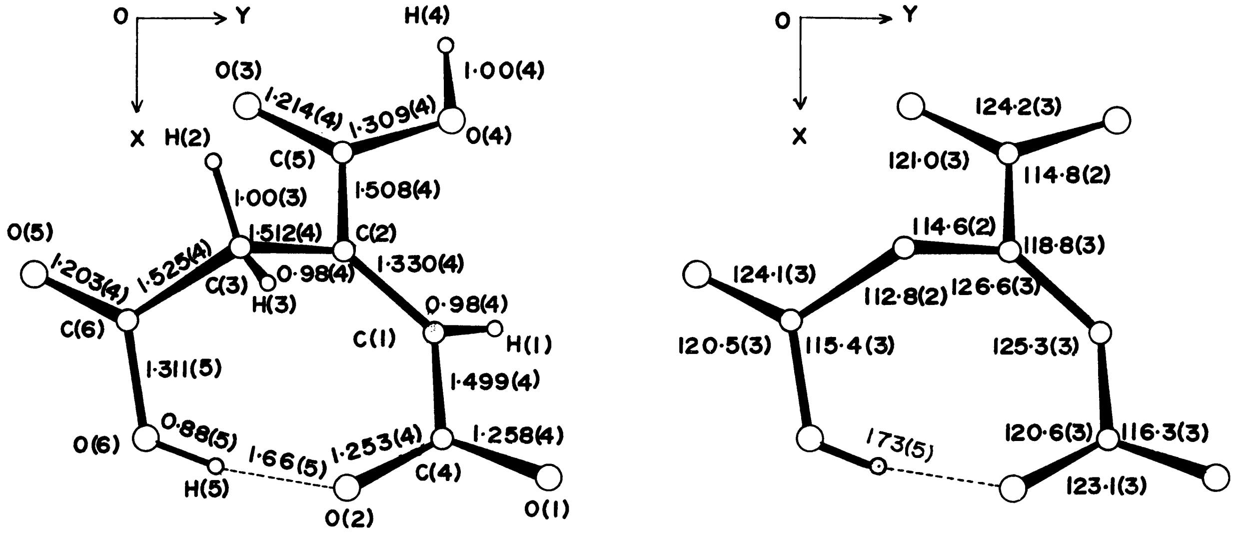

Fig. 2. Bond lengths(Å) and angles(degrees) in the *trans*-aconitate ion. The e.s.d's are indicated in parentheses with respect to the least significant digit.

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*After completion of this work, we learned about the determination of structure of the title compound by Dargay *et al.*; J. M. Dargay, H. M. Berman, H. L. Carrell and J. P. Glusker, Acta Cryst., **B28** (1972), in the press.

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