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Original Scientific Paper

The Two Fundamental H-Bond Types in Acid Salts Displayed in the Dimorphs of Potassium Hydrogen Tartronate

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At ambient temperature the acid potassium salt of tartronic acid crystallizes in two forms. The α form is monoclinic, space group $P2_1/n$ with $a = 7.356$, $b = 8.116$, $c = 9.197$ Å, $\beta = 94.81^0$ and $Z = 4$. The β form is also monclinic, space group $P2_1/c$ with $a = 6.532$, $b = 9.248$, $c = 9.505$, $\beta = 99.74^0$ and $Z = 4$. The α and β structures were solved by Patterson and Fourier methods and refined to $R = 0.047$ with 1129 and 1204 observed diffractometer data respectively. The fundamental differences in structural aspects between the dimorphs of this acid salt are found in the H-bond schemes. In the α form the carboxyl groups are coupled by A-type H bonds, in the β form by H bonds of the B type.

INTRODUCTION

The strong hydrogen bonds between carboxyl groups occurring in acid salts of carboxylic acids can be classified into two groups; according to Speakman[1] the different types are termed A and B. A-type hydrogen bonds connect carboxyl groups that the are related by translational-free symmetry. In B-type bonds the linked carboxyl groups are crystallographically independent. There has been a prolonged discussion whether A-type bonds are genuinly symmetrical. In some cases[2] it may be suspected that disorder provokes an apparent symmetrical situation. The crystallographic evidence as to the occurrence of two fundamental types of hydrogen bonds in acid salts is paralleled by IR studies. In that respect we refer to the classic paper of Hadži[3], who has made important contributions in this field.

In a preliminary account we reported on the dimorphism of the acid potassium salt of tartronic acid[4]. The two forms α and β crystallize in the same space group, but the α form exhibits A-type hydrogen bonds, whereas in the β form a B-type hydrogen bond is present.

EXPERIMENTAL

The crystals first obtained were grown from an ethanol-water solution and appeared to be of the α form. Later attempts to again crystallize this modification were not successful. Perhaps the α form is metastable and its crystallization is prevented by germs of the β form, prepared later on in the laboratory. Crystals of the latter form were obtained by evaporation of an aqueous solution.

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* Festschrift of Professor Dušan Hadži.

Crystal Data

$C_3H_3O_5K$, $M_r = 158.15$. Monoclinic.

α form: $a = 7.356$, $b = 8.116$, $c = 9.197$ Å, $\beta = 94.81^0$, $V = 457.1$ Å^3, $Z = 4$, $d_X = 1.92$ g cm^{-3}. Space group $P2_1/n$. μ (MoKα) = 0.97 mm^{-1}.

β form: $a = 6.532$, $b = 9.248$, $c = 9.505$, Å, $\beta = 99.74^0$, $V = 565.9$ Å, $Z = 4$, $d_X = 1.86$ g cm^{-3}. Space group $P2_1/c$. μ (MoKα) = 0.94 mm^{-1}.

All X-ray measurements took place on an Enraf-Nonius CAD-3 diffractometer using Zr-filtered MoKα radiation ($\lambda = 0.7101$ Å). A tetartosphere of the reciprocal lattice was measured up to $\vartheta = 27.5^0$ in the ω-scan mode the intensities of 1129 (α form) and 1204 (β form) reflections were collected. They were corrected for Lorentz-polarization factors and for absorption.

STRUCTURE DETERMINATION AND REFINEMENT

In both structures the potassium ion positions were located by Patterson analysis. The determination of the C and O atoms proceeded by standard heavy-atom methods. The locations of all H atoms were clearly shown in subsequent difference Fourier maps.

TABLE I

*Final Atomic Parameters (Standard Deviations in Parentheses) of the α and β Modifications of Potassium Hydrogen Tartronate**

For the non-hydrogen atoms, the coordinates and β_{ij} values are × 10^4; for the hydrogen atoms the coordinates are × 10^3. The anisotropic temperature factors are of the form $\exp -(\beta_{11} h^2 + \beta_{22} k^2 + \beta_{33} l^2 + 2\beta_{12} hk + 2\beta_{23} kl + 2\beta_{31} hl)$.

α Modification

	x	y	z	β_{22}	β_{11}	β_{33}	$2\beta_{12}$	$2\beta_{23}$	$2\beta_{31}$
K(1)	3417(1)	777(1)	3062(1)	97(1)	145(1)	104(1)	41(2)	—40(2)	47(2)
O(2)	5841(3)	713(3)	1007(2)	130(4)	213(5)	58(2)	—134(8)	—21(6)	14(5)
O(3)	8074(3)	1051(3)	—462(2)	130(4)	195(5)	55(2)	16(8)	22(6)	19(5)
O(4)	9977(3)	596(3)	3783(2)	95(4)	228(6)	74(3)	40(7)	103(6)	37(5)
O(5)	7128(3)	1339(3)	4075(2)	107(4)	201(5)	72(3)	—8(7)	1(6)	71(5)
O(6)	10219(3)	2603(3)	1526(2)	127(4)	139(4)	75(3)	—92(7)	5(5)	62(5)
C(7)	7401(3)	1236(4)	699(3)	104(5)	99(5)	59(3)	8(8)	31(6)	—6(6)
C(8)	8450(3)	2212(3)	1923(3)	93(5)	91(5)	65(3)	—12(8)	—8(6)	27(6)
C(9)	8482(3)	1340(4)	3383(3)	87(4)	110(5)	50(3)	—32(8)	—23(6)	10(6)
H(10)	765(5)	310(5)	200(5)	$B = 3$ Å^2					
H(11)	1030(5)	215(5)	70(5)	3					
H(12)	1/2	0	0	5					
H(13)	1	0	1/2	5					

β Modification

	x	y	z	β_{22}	β_{11}	β_{33}	$2\beta_{12}$	$2\beta_{23}$	$2\beta_{31}$
K(1)	2192(1)	3448(1)	4419(1)	126(2)	58(1)	65(1)	18(2)	—13(1)	—29(2)
O(2)	8955(4)	1978(3)	2687(3)	146(7)	89(4)	148(5)	88(9)	—123(7)	—158(9)
O(3)	6319(4)	1360(3)	986(2)	158(7)	59(3)	63(3)	11(7)	—33(5)	—40(7)
O(4)	6615(4)	5663(3)	1231(3)	230(8)	61(3)	72(3)	—75(9)	37(5)	—96(8)
O(5)	8879(4)	5071(2)	3173(2)	112(6)	56(3)	74(3)	—37(7)	14(5)	—54(6)
O(6)	3948(3)	3584(3)	1727(2)	85(5)	64(3)	71(3)	3(7)	6(5)	—33(6)
C(7)	7102(5)	2159(3)	1947(3)	111(8)	45(4)	57(4)	—9(9)	—2(6)	—15(9)
C(8)	6019(4)	3478(3)	2431(3)	90(7)	52(4)	42(3)	—8(9)	—6(6)	—16(8)
C(9)	7251(5)	4855(3)	2243(3)	117(8)	48(4)	49(3)	—10(9)	—18(6)	7(8)
H(10)	600(8)	335(5)	345(5)	$B = 3$ Å^2					
H(11)	395(8)	410(5)	90(5)	3					
H(12)	985(8)	120(5)	225(5)	5					

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* A Table of observed and calculated structure factors can be obtained from the Library of the *Croatica Chemica Acta*, Marulićev trg 19, 41000 Zagreb Yugoslavia.

Block-diagonal refinements of the complete structures (anisotropic for the non-H atoms and with isotropic thermal parameters for the H atoms set equal to the isotropic equivalent of the atom to which they are bound) converged to $R = 0.047$ for both structures. In both refinements an extinction parameter[5,6] was adapted; values of $290 \cdot 10^{-4}$ (α form) and $34 \cdot 10^{-4}$ cm^{-1} (β form) were obtained for the quantity $r\,[1 + r^2/(\lambda g)^2]^{-1/2}\,(e^2/mc^2)^2\,\lambda^2/V^2$. Scattering factors were calculated by means of the analytical expression of Moore[7]. The final parameters are listed in Table I.

DISCUSSION

Molecular geometry

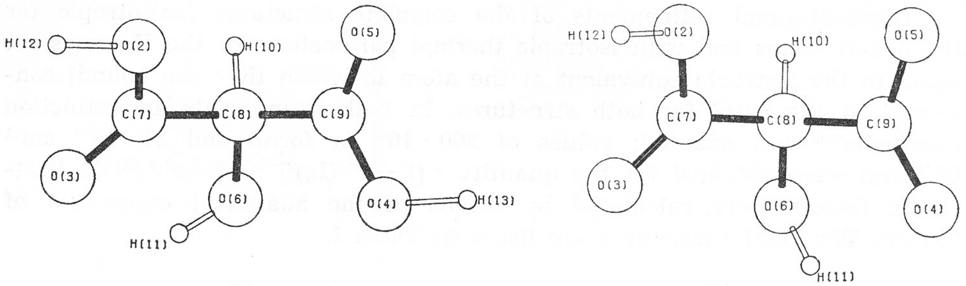
Bond lengths and bond angles are listed in Table II. The conformations of the tartronic acid molecules in the dimorphs and the numbering scheme used in the text are shown in Figure 1. Some selected torsional angles are

TABLE II

Bond Lengths (Å) *and Bond Angles* (⁰) *of the Tartronic Acid Molecules in the* α *and* β *Modifications*

	α Form	β Form
C(7)—O(2)	1.277(3)	1.304(4)
C(7)—O(3)	1.223(3)	1.218(4)
C(9)—O(4)	1.281(3)	1.233(4)
C(9)—O(5)	1.226(3)	1.278(4)
C(8)—O(6)	1.417(3)	1.408(3)
C(7)—C(8)	1.531(4)	1.520(4)
C(8)—C(9)	1.516(4)	1.533(4)
O(2)—H(12)*	1.216(2)	1.06 (5)
O(4)—H(13)*	1.218(2)	
O(6)—H(11)	0.85 (4)	0.92 (5)
C(8)—H(10)	0.94 (4)	0.98 (5)
C(7)—O(2)—H(12)*	113.5(2)	114 (3)
C(9)—O(4)—H(13)*	113.4(2)	
C(8)--O(6)—H(11)	106 (3)	108 (3)
O(2)—C(7)—O(3)	126.1(3)	124.1(3)
O(2)—C(7)—C(8)	114.6(2)	112.1(3)
O(3)—C(7)—C(8)	119.3(2)	123.8(3)
O(6)—C(8)—C(7)	110.1(2)	111.8(2)
O(6)—C(8)—C(9)	112.7(2)	111.6(2)
O(6)—C(8)—H(10)	116 (2)	108 (3)
C(7)—C(8)—C(9)	112.3(2)	110.5(2)
C(7)—C(8)—H(10)	100 (3)	107 (3)
C(9)—C(8)—H(10)	105 (3)	108 (3)
O(4)—C(9)—O(5)	124.5(3)	125.1(3)
O(4)—C(9)—C(8)	115.1(2)	118.7(3)
O(5)—C(9)—C(8)	120.5(2)	116.2(3)

* In the α form atoms H(12) and H(13) are put at special positions.



(a) (b)

Figure 1. Key to the atomic numbering of the tartronate anions; α form (a), β form (b).

given in Table III. They concern the conformational arrangement of the carboxyl groups with respect to the bonds C(8)—O(6). From statistical studies[8,9] it appears that a *synperiplanar* conformation about the C(sp^2) — C(sp^3) bond is predominant in α-hydroxy acetic acid moieties. However, in the α modification the less favourable *antiperiplanar* conformation is found for one of the carboxyl groups.

TABLE III

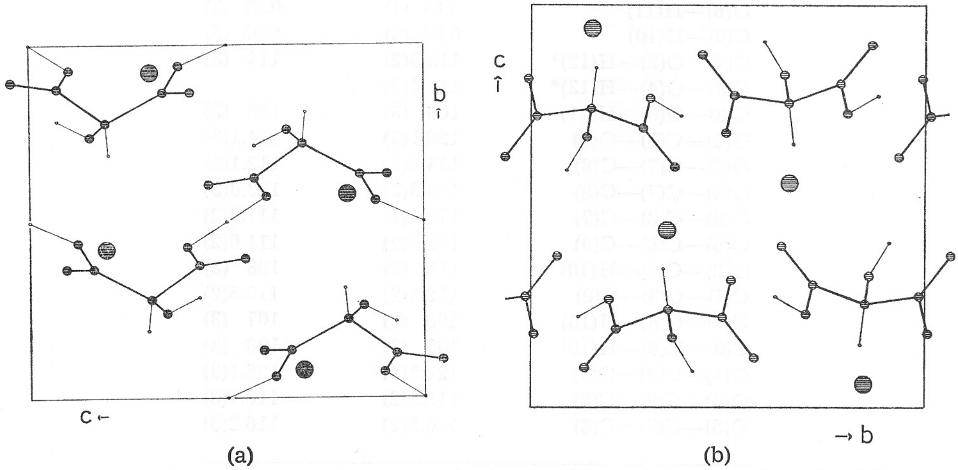
Torsion Angles About the C(sp^2)—C(sp^3) *Bonds* (°)

	α from	β from
O(3)=C(7)—C(8)—O(6)	—6.8(4)	5.4(4)
O(5)=C(9)—C(8)—O(6)	158.9(3)	—21.4(4)*

* In the calculation of this value O(5) is replaced by O(4) as in this carboxylate group C(9)—O(4) appears to have the greater double-bond character.

Structural aspects

Projections of the structures along [100] are shown in Figures 2a and b. The potassium ions are eightfold coordinated by oxygen atoms in an irregular



(a) (b)

Figure 2. Projections of the structures of potassium hydrogen tartronate along the [100] axes; α form (a), β form (b).

way which is characteristic for this kind of cations. The mean K ... O distances in the α and β form are 2.89 and 2.86 Å respectively.

The striking difference between the dimorphs is the hydrogen-bond scheme, the α form having A-type bonds, whereas in the β form a B-type bond is present. H-bond geometries are given in Table IV. In the α form single peaks of electron density located at the centres of the two independent H bonds were found. In Table IV also two geometries of possible H bonds (one being *intra*molecular) involving the aliphatic hydroxyl group are included. However, these arrangements must be described as being at best weak bifurcated H bonds. The O—H ... O angles concerned would take on very extreme positions in the H-bond angle distribution reported in a statistical study[10] on H-bond geometries in crystals (*viz.* considerably higher than the 1 kcal limit above which an H-bond parameter rarely is observed). In contrast with the α form in the β form the aliphatic hydroxyl group unmistakably acts as a proton donor and links two anion chains propagating along the screw axes. As can be inferred from Table IV in this structure the possible *intra*molecular H-bond interaction with the carboxyl group is even more unfavourable than it is already in the α form. The carboxylgroup coupling in the β modification follows the B-type scheme. We therefore see that the two fundamental H-bond types are represented in the crystal structures of one and the same compound. Glide planes interrelate the anion chains in both modifications.

TABLE IV

Hydrogen-bond Geometries (Distances in Å, Angles in Degrees)

Small letters indicate symmetry operations: (a) $1-x, -y, -z$; (b) $2-x, -y, 1-z$; (c) $1/2+x, 1/2-y, -1/2+z$; (d) $2-x, -1/2+y, 1/2-z$; (e) $1-x, 1-y, -z$.

D	H	*A*	*D*···*A*	*D*—H	H···*A*	*D*—H···*A*
α form						
O(2)	H(12)	O(2a)	2.433(4)	1.216(2)	1.216(2)	180
O(4)	H(13)	O(4b)	2.436(4)	1.218(2)	1.218(2)	180
O(6)	H(11)	O(5c)	2.885(4)	0.85 (5)	2.42 (5)	114(3)
O(6)	H(11)	O(3)	2.634(4)	0.85 (5)	2.08 (5)	122(3)
β form						
O(2)	H(12)	O(5d)	2.484(3)	1.06 (5)	1.43 (5)	173(3)
O(6)	H(11)	O(4e)	2.859(3)	0.92 (3)	2.01 (5)	153(3)
O(6)	H(11)	O(4)	2.689(3)	0.92 (3)	2.24 (5)	109(3)

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IZVLEČEK

Kalijev hidrogen tartronat: dva osnovna tipa H-vezi

Jan Kroon in Jan A. Kanters

Pri sobni temperaturi kisla sol tartronske kisline kristalizira v dveh kristalnih oblikah. α oblika je monoklinska, prostorska skupina $P2_1/n$ z $a = 0.7356$, $b = 0.8116$, $c = 0.9197$ nm, $\beta = 94.81^0$ in $Z = 4$. β oblika je tudi monoklinska, prostorska skupina $P2_1/c$ z $a = 0.6532$, $b = 0.9248$, $c = 0.9505$ nm $\beta = 99.74^0$ in $Z = 4$. Kristalni strukturi α in β oblike sta bili rešeni po Pattersonovi in Fourierjevi metodi in izpiljeni z R vrednostjo 0.047 za 1129 in 1204 uklonov izmerjenih z difraktometrom.

V splošnem ločimo pri kislih soleh karboksilnih kislin A in B tip vodikovih vezi. Pri A-tipu sta karboksilni skupini, ki sta udeleženi v vodikovi vezi simetrijsko odvisni, medtem ko sta pri B-tipu karboksilni skupini kristalografsko popolnoma neodvisni. Zanimivost zgornjih dveh strukturnih določitev je v tem, da pri α obliki kalijevega hidrogen tartronata nastopajo vodikove vezi A-tipa, pri β obliki pa vodikove vezi B-tipa.