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The Structure of Potassium Hydrogentartrate: A Combined X-ray, Semiempirical, and Ab Initio Study

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ABSTRACT: *Single crystals of potassium hydrogentartrate, (2R,2R)-$KO_2C(CHOH)_2CO_2H$, were taken from a three-year-old wine bottle. The structure was determined by low-temperature single-crystal X-ray diffraction analysis using a Siemens SMART diffractometer. (2R,2R)-$KO_2C(CHOH)_2CO_2H$ crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z = 4$ and unit cell dimensions $a = 7.6065(5)$, $b = 7.7599(5)$, and $c = 10.6054(7)$ Å. The structure of an isolated hydrogentartrate anion, (2R,2R)-$[O_2C(CHOH)_2CO_2H]^-$, was calculated at the semiempirical AM1 and PM3 levels of theory with a VSTO-3G* basis set and in addition ab initio at the self-consistent level of theory using a standard 6-31G(d,p) basis set (Non-SI units employed: kcal ≈ 4.184 kJ, Å = 10^{-10} m).* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:307–310, 1998

INTRODUCTION

Although the structures of potassium hydrogentartrate [1] and, more recently, sodium hydrogentartrate monohydrate [2] have been determined previously, we decided to reinvestigate the potassium hydrogentartrate structure experimentally (X-ray) and to calculate at semiempirical and ab initio level the structure of the anion. The $C_4O_6H_5^-$ anion that contains highly polarized bonds seems to be a good candidate to compare and contrast experimental data with calculated values obtained from both semiempirical and more expensive ab initio computations. Especially the frequency analyses at SCF level to characterize the nature of the stationary point found require far more CPU time than those done at PM3 or AM1 level. The results obtained give credence to those calculated values for unstable C/O/H, B/O/H, and N/O/H compounds for which reliable high-quality experimental data are not easily available. For example, the tartrate dianion $O_2C(CHOH)_2CO_2^-$ is isoelectronic with the neutral molecule $O_2N(CHOH)_2NO_2$. An account of this work is given below.

EXPERIMENTAL

Materials

Single crystals of very high-quality potassium hydrogentartrate, (2R,2R)-$KO_2C(CHOH)_2CO_2H$, were taken from a three-year-old wine bottle (Adam von Itzenstein, Rheingau, 1994 Hallgartener Jungfer,

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TABLE 1 Selected Measured (X-ray) and Computed (AM1/VSTO-3G*, PM3/VSTO-3G*, RHF/6-31G*) Bond Lengths (Å) and Angles (°) of (2R,2R)-$KO_2C(CHOH)_2CO_2H$ and $[O_2C(CHOH)_2CO_2H]^-$

	X-ray	*AM1/VSTO-3G**	*PM3/VSTO-3G**	*RHF/6-31G**
K1–O1	2.710(1)			
K1–O2	2.993(2)			
K1–O3	2.937(1)			
K1–O4	2.777(1)			
K1–O6	2.872(1)			
C1–C2	1.519(3)	1.52	1.56	1.516
C1–O1	1.213(2)	1.23	1.22	1.186
C1–O2	1.322(2)	1.37	1.36	1.343
C2–O3	1.434(2)	1.41	1.41	1.390
C2–C3	1.531(3)	1.54	1.56	1.541
C3–O4	1.413(2)	1.41	1.41	1.401
C3–C4	1.535(3)	1.56	1.58	1.550
C4–O5	1.274(2)	1.27	1.27	1.249
C4–O6	1.249(2)	1.25	1.24	1.219
O1–K1–O3	57.8(1)			
C2–C1–O1	124.3(2)	131.7	132.5	128.1
C1–C2–O3	110.8(2)	113.2	107.9	108.9
K1–O3–C2	115.2(1)			
K1–O1–C1	125.1(1)			
C1–C2–C3	109.4(1)	110.5	110.7	110.4
O2–C1–C2	111.3(1)	113.2	114.7	111.0
C2–C3–C4	108.2(1)	108.3	108.2	107.2
C3–C4–O5	117.6(1)	114.5	116.1	112.1
C3–C4–O6	117.6(2)	119.0	119.9	117.4
O5–C4–O6	124.7(2)	126.6	123.9	130.4
O4–C3–C4	113.4(1)	110.7	111.3	110.5

Riesling, Spätlese, trocken; Vereinigte Winzergenossenschaft, Hallgarten, D-65375 Oestrich-Winkel) and were washed with 1 mL of cold water, 1 mL of cold ethanol, 1 mL of ether, and three times with 5 mL $CFCl_3$.

CHN analysis (188.18): found C 25.4, H 2.7, N 0.0%; calcd C 25.53, H 2.68, N 0.00%.

X-ray Structure Determination of (*2R,2R*)-$KO_2C(CHOH)_2CO_2H^-$

Crystal Data. Potassium hydrogentartrate, (2R,2R)-$KO_2C(CHOH)_2CO_2H$, M = 188.18, orthorhombic, a = 7.6065(5), b = 7.7599(5), and c = 10.6054(7) Å; U = 625.99(7) $Å^{-3}$, space group $P2_12_12_1$, Z = 4, D_c = 1.997 g cm^{-1}. Crystal dimensions 0.15 × 0.15 × 0.20 mm. $\mu(\text{Mo-}K_\alpha)$ = 0.83 mm^{-1}, λ = 0.71073 Å, $F(000)$ = 384.

Data Collection and Processing. Siemens SMART diffractometer, −100°C, ω scan mode, $2\theta_{max}$ = 60.0°, graphite monochromated Mo-K_α radiation, 4539 measured reflections, 1794 unique reflections, 1621 reflections with $[I_{net} > 2.5\ \sigma\ I_{net}]$. Absorption corrections were made using SADABS.

Structure Analysis and Refinement. The structure was solved by direct methods, and all atoms (including the hydrogen atoms) were refined anisotropically. Refinement was by least-squares to R_F = 0.027, ($R_F = \Sigma[F_0 - F_c]/\Sigma[F_0]$), R_W = 0.026, (R_W = Sqrt.$[\Sigma\{w[F_0 - F_c]^2\}/\Sigma\{wF_0^2\}]$), and GoF = 1.40 for significant reflections; R_F = 0.034 and R_W = 0.028 for all reflections. In the last D-map, the deepest hole was −0.26 $eÅ^{-3}$, and the highest peak was 0.34 $eÅ^{-3}$. Computations were carried out using the NRCVAX program system and published scattering factors [3–5].

Further details of the crystal structure determinations are available upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-406972, the names of the authors, and the journal citation.

Semiempirical PM3 Computations. All calculations were carried out with the program package HyperChem [6] at the semiempirical AM1 and PM3 [7] levels of theory using a VSTO-3G* basis set. We

TABLE 2 AM1, PM3, and RHF Calculated Energies, Zero-Point Energies, and Partial Charges for (2R,2R)-$[O_2C(CHOH)_2CO_2H]^-$

	*AM1/VSTO-3G**	*PM3/VSTO-3G**	*RHF/6-31G**
E	-1617.8 kcal mol^{-1a}	-1612.7 kcal mol^{-1a}	-603.61261 a.u.
NIMAG^b	0	0	0
zpe / kcal mol^{-1}	66.3	64.8	70.8
q(O1) / e	-0.38	-0.41	-0.72
q(O2) / e	-0.34	-0.33	-0.57
q(O3) / e	-0.34	-0.39	-0.79
q(O4) / e	-0.35	-0.32	-0.79
q(O5) / e	-0.58	-0.64	-0.77
q(O6) / e	-0.53	-0.56	-0.71

[a] E^{AM1} and E^{PM3}, for definition, see Ref. [6].
[b] NIMAG = number of imaginary frequencies.

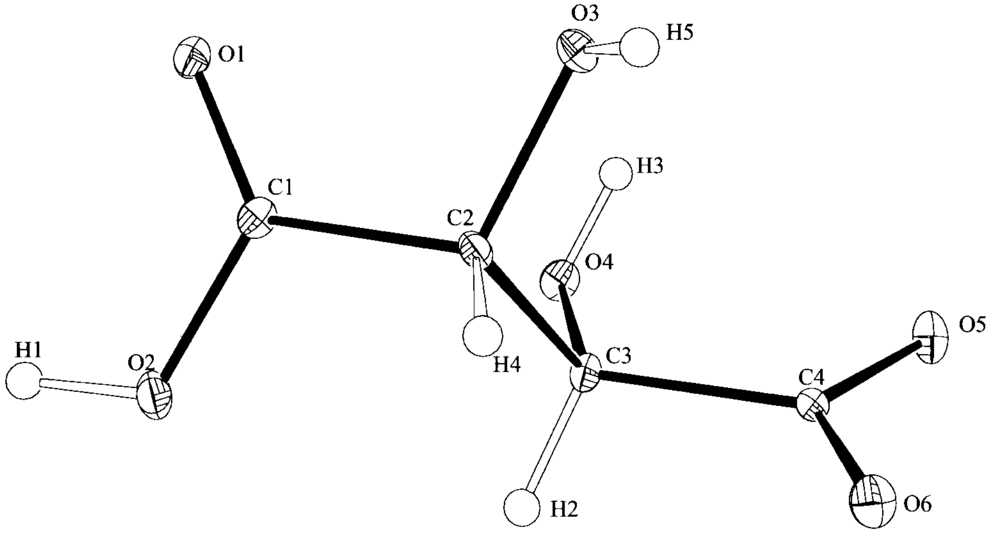

FIGURE 1 The molecular structure and atomic labeling scheme of the anion [(2R,2R)-$O_2C(CHOH)_2CO_2H]^-$ (ORTEP representation [5]).

chose PM3 in addition to AM1 (which differs from AM1 [8] only in the values of the parameters) since the parameters for PM3 were derived by comparing a much larger number and wider variety of experimental versus computed molecular properties. The PM3 is a reparameterization of AM1, which is based on the neglect of diatomic differential overlap (NDDO) approximation. NDDO retains all one-center differential overlap terms when Coulomb and exchange integrals are computed.

Ab Initio Computations. The structure, energy, vibrational frequencies, and zero-point energy of an isolated hydrogentartrate ion, (2R,2R)-$^-O_2C(CHOH)_2CO_2H$, were computed ab initio (C_1 symmetry) and fully optimized at the RHF level of theory with the program package Gaussian 94 [9]. For H, C, and O, a standard 6-31G(d,p) basis set was used [10].

RESULTS AND DISCUSSION

The structure of potassium hydrogentartrate, (2R,2R)-$KO_2C(CHOH)_2CO_2H$, was determined experimentally by X-ray diffraction analysis. A diagram showing the molecular structure of the anion is given in Figure 1. As illustrated in Figure 2, there are eight short contacts between the potassium atom and the anions in the range of 2.7–3.2 Å (cf. sum of ionic radii of $K^+_{CN=8}$ and $O^{2-}_{CN=4}$ = 2.89 Å) [11]. The potassium ions are coordinated by the eight O atoms at the corners of a distorted square antiprism. As is usual, the coordination geometry of the K^+ ion is very irregular (cf. Refs. [12,13]). It is also important

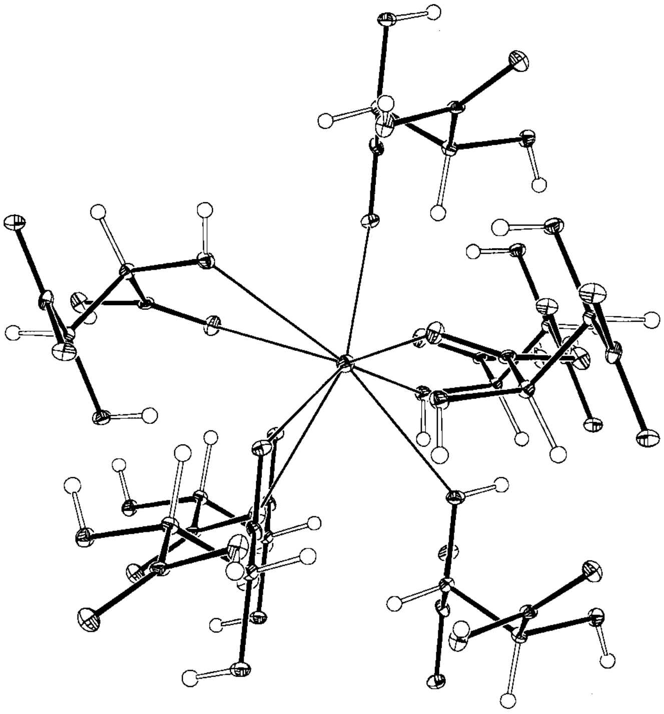

FIGURE 2 Cation–anion interactions in (2R,2R)-$KO_2C(CHOH)_2CO_2H$ in the range between 2.7 and 3.2 Å (ORTEP representation [5]).

to stress that in the solid state there are strong hydrogen bonds bridging the tartrate anions (cf. Figure 2). The crystal lattice of the title compound is formed by layers of hydrogen-bonded tartaric anions separated by layers of K^+ ions. The H bonds between the carboxyl and carboxylate groups are, however, rather long with O. . .O 2.53 Å. A very similar coordination geometry has also been observed in the sodium hydrogentartrate [2]. Table 1 summarizes the most important experimentally obtained structural parameters for $K^+[O_2C(CHOH)_2CO_2H]^-$. Table 1 also contains the results obtained from an ab initio calculation (see below). In contrast to previous studies [1,2], we investigated the potassium hydrogentartrate as anhydrate, whereas it is often found to be the monohydrate [2]. However, the previous low-temperature structure determination of an anhydrate form is of comparable quality [1a].

The structure for an isolated [(2R,2R)-$O_2C(CHOH)_2CO_2H]^-$ anion (gas phase) was fully optimized without any symmetry constraints (C_1 symmetry) at the semiempirical AM1 and PM3 levels and at the self-consistent field level (Table 1). The stationary points found (Table 2) were shown to represent true minima on the potential energy hypersurface at all levels of theory applied. The calculated Mulliken charges are also summarized in Table 2.

In conclusion, the quantummechanically calculated structure for an isolated (2R,2R)-$[O_2C(CHOH)_2CO_2H]^-$ anion (gas phase) closely resembles the situation found in the solid state. The results obtained from the semiempirical AM1 and PM3 calculations are of comparable quality to those obtained from an ab initio RHF computation.

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