ditional studies are in progress to further characterize the thermochromism, the solution equilibrium, and the mechanism of the $^{119}Sn-^{117}Sn$ scalar coupling in **1**.

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Deltic Acid, a Novel Compound

Dag Semmingsen*

Institutt for Matematikk og Naturvitenskap
Høgskolesenteret i Rogaland
4000 Stavanger, Norway

Per Groth

Kjemisk Institutt, Universitetet i Oslo
0315 Oslo 3, Norway

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Owing to their simplicity and attractive chemical structures, the cyclic oxocarbon acids ($C_nO_nH_2$) and their conjugate bases, the oxocarbon anions $(C_nO_n)^{2-}$, have been the subject of a number of experimental and theoretical investigations over the past several years.[1-3] In particular it has been suggested that the oxocarbon anions constitute a series of aromatic compounds.[4] Although this proposition has been questioned for the oxocarbons in general,[5] there are theoretical arguments in favor of such a conception in case of the smallest member of the oxocarbon anions, the deltate ion.[5,6]

While the structures of the other oxocarbon ring systems are fairly well documented,[7-11] no structure determination of the novel ring system in deltic acid has hitherto been reported. However, thorough investigations of the deltate ion[12] and deltic acid[13] by IR and Raman methods have been reported. Deltic acid and its lithium salt were first prepared by Eggerding and West[14] in 1976 by a method similar to that by Dehmlow,[15] and more recently in a total synthesis by Pericâs and Serratosa,[16] and is not easily accessible. In aqueous solutions deltic acid hydrolyzes with a ring opening, and although the deltate ion appears to be somewhat more stable and crystalline salts have been reported, crystals suitable for structural studies are difficult to obtain.[14] We wish to report the molecular and crystal structure of deltic acid as determined by X-ray analysis.

A sample of the di-*tert*-butyl ester of the acid was kindly supplied by Professor Serratosa, and crystals were grown from alcohol after direct crystal growth by slow hydrolysis of the ester in neat trifluoroacetic acid had failed. A crystal of the compound was subjected to a low-temperature X-ray analysis at the University of Oslo.[17]

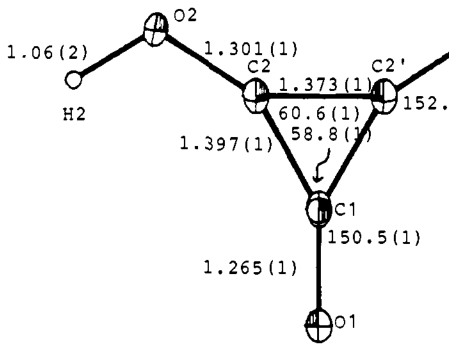

Figure 1. The deltic acid molecule with atom nomenclature: bond lengths (Å), left, and angles (deg), right. Estimated standard deviations in parenthesis.

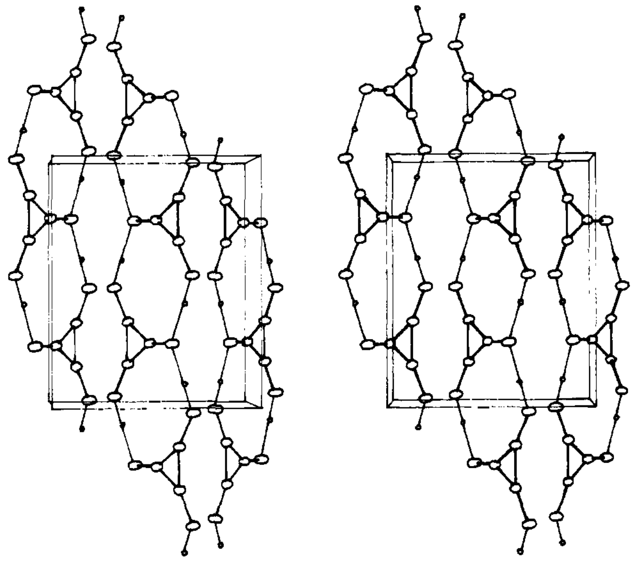

Figure 2. Stereo view of the unit cell.

Bond lengths and angles are shown in Figure 1, while the arrangement of the molecules in the crystal is shown in Figure 2. The crystal structure of deltic acid corresponds closely to the model surmised by Lautié et al. on the basis of their IR and Raman spectroscopic investigation. The molecules are situated across a mirror plane in the crystal and thus have C_{2v} symmetry. They are tied together in strings in the (120)-planes in a "dimeric" fashion resembling the well-known dimeric carboxylic acid units. However, each carbonyl group accepts two equivalent, strong hydrogen bonds ($r(O\cdots O) = 2.555$ (1) Å), which are almost perfectly linear ($<O-H\cdots O = 178.4°$). We find it unusual that a carbonyl group in a neutral molecule accepts two hydrogen bonds of this strength.

Although the molecular geometry clearly is that of 2,3-dihydroxycyclopropen-1-one, the covalent bond lengths in deltic acid show a remarkable degree of conjugation. As was found in squaric acid, the high degree of symmetrization of the molecule is at least partly due to the strong hydrogen bonding in the crystal. At least two other discernible factors influence the overall geometry of the

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(17) X-ray analysis of deltic acid (2,3-dihydroxycyclopropen-1-one): space group *Pnam* (nonstandard for *Pnma*); unit cell, $a = 6.173$ (1) Å, $b = 6.520$ (1) Å, $c = 7.899$ (2) Å; $d_{calcd} = 1.80$ g/cm^3; Intensity measurements were made with $3° < 2\theta < 90°$ by using graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at 135 K on a Nicolet P3/F diffractometer; 1015 unique reflections; solved by direct methods; hydrogen atom located in difference Fourier map; full-matrix least-squares refinements; $R = 0.034$, $R_w = 0.042$, $S = 2.26$.

molecule; a larger contribution of dipolar resonance forms in deltic acid than in the other oxocarbon acids and the tremendous amount of strain associated with the three-membered ring system.

Compared with squaric acid both the C—O and the C=O bonds have been considerably enlarged: the former with 0.010 Å and the latter with 0.036 Å. Their difference, 0.036 Å, is very small compared to that in squaric acid of 0.062 Å. A detailed comparison of the intra ring bonds in the two molecules is not warranted due to the difference in angle strains and the incompatibility of the structural details in the two molecules. However, the difference in bond lengths between the nominal C-C single and the C=C double bonds is rather small (0.024 Å) in deltic acid, compared with the two similar bonds in squaric acid (0.048 Å). We take the above as evidence for a lower bond order in the C–O bonds but a higher overall conjugation in deltic acid than in squaric acid.

The influence of hydrogen bonding and metal complexion on the geometry of diphenylcyclopropenone has recently been discussed by Ng et al.,[18] who argue that a substantial symmetrization of bond lengths and angles takes place when the lone pairs of the carbonyl engage in such bonding. Their view is that there is an enhancement of aromatic cyclopropenylium mesomeric forms to the structure when the carbonyl lone pairs are involved in hydrogen bonding and donation. In fact, intra ring bond lengths and angles in deltic acid do not deviate significantly from their results on the Sn adduct of diphenylcyclopropenone, though the exocyclic C=O bond in deltic acid is much longer (0.026 Å) than that found in their work.

A different view is advocated by Allen[19] in his review of available data on cyclopropene derivatives. He claims that there is little or no contribution from dipolar or aromatic resonance forms to the structures of these materials. The observed symmetrizations have a similar origin to the bond length alterations found in substituted cyclopropanes and are a result of a change in hybridization at C1 which provides stronger σ-overlap and therefore strengthens the vicinal C–C single bond. In addition there is a shortening due to π-donation from the carbonyl group which also produces a lengthening of the distal C=C bond. The combined effect should amount to 0.080 Å in the single bond in cyclopropenone and reduce this bond to about 1.424 Å which is still longer than 1.397 Å in deltic acid. The intra ring double bond should increase to 1.346 Å, much shorter than 1.373 Å in deltic acid. We therefore think that there may be significant contributions from dipolar and/or cyclopropylium resonance forms to the deltic acid structure in the solid state.

Further arguments for the presence of dipolar resonance forms in deltic acid come from theoretical calculations; recent semiempirical calculations indicate that the deltate di-ion is unique among the oxocarbon ions in having a high degree of aromatic character, because the ion can be regarded as a symmetrically trisubstituted cyclopropylium ion.[5,6] Taking the argument further this suggests that deltic acid is more "aromatic" than squaric acid. For squaric acid we have found that the average values of the C–O and C–C bonds in the molecule closely correspond to the bond values in a hydrogen bonded and, within the limits of error, fourfold squarate ion.[20] If this carries over to the deltic acid system, the C–O and C–C bond lengths will be 1.289 and 1.389 Å, respectively. The latter is somewhat longer than 1.373 Å cited for the cyclopropenium ion[21] but certainly shorter than the value of this bond (1.42 Å) in symmetrical π-complexes of cyclopropylium.[19,22]

Now that the structure of deltic acid has become known, the effect of ionization on the geometry of this interesting ring system can begin to be assessed. We hope to report on these matters at a later date.

Registry No. Deltic acid, 54826-91-4.

Supplementary Material Available: Listings of crystal data, atomic positions, and anisotropic temperature factors (1 page); listings of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Additions and Corrections

Geometric Equivalents of Enantiomers in Studies of the Stereochemical Course of Substitution at Carbon. Electronic Effects in Nucleophilic Addition to Carbonyl Groups and to Carbocations. Virtual Proof of the Existence of σ Participation by Unstrained Carbon–Carbon Bonds [*J. Am. Chem. Soc.* **1986**, *108*, 1598]. C. K. CHEUNG, L. T. TSENG, M.-H. LIN, S. SRIVASTAVA, and W. J. LE NOBLE*

Page 1600: In Table I, all three *E* and *Z* entries for the 5-substituent OH need be reversed: 57% *E* and 43% *Z*.

Page 1599–1600: The last sentence beginning on 1599 and continuing onto 1600 should be stricken.

Unique Spectroscopic Properties of Mixed-Ligand Complexes with 2,2′-Dipyridylamine: A Dual Luminescence from a Ruthenium(II) Complex [*J. Am. Chem. Soc.* **1987**, *109*, 4895–4901]. RICHARD L. BLAKLEY and M. KEITH DEARMOND*

Page 4898, Table II: The lifetime of the single emission for $[Ru(bpy)(HDPA)_2]^{2+}$ at 77 K in H_2O should read 2.54 ± 0.89 μs (not 254 ± 0.89 μs). The two wavelengths of detection used to monitor the emission lifetime of $[Ru(bpy)_3]^{2+}$ at 77 K in EtOH were 578 (m) and 628 (sh) (not 328).