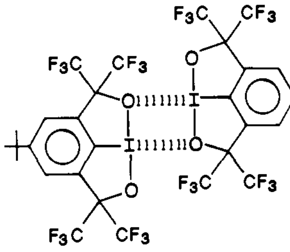
do-octahedral ($AX_2Y_2E_2$) with the four ligands essentially square planar and the two lone pairs anti with respect to each other. Coordination around each phosphorus is tetrahedral (distorted) with two long P–O bond[14] lengths of around 1.62 Å each and two shorter ones of about 1.47 Å each. The remaining structural features (i.e., olefin, *t*-Bu, Ph, etc.) are unexceptional. These novel structural features around the iodines and phosphorus are due to the dimeric nature and consequent secondary bonding interactions[8] in the solid state of the molecule. In particular, both the intra- and intermolecular I–O bond distances are of the same order of magnitude (2.70–2.85 Å)[15] but significantly less than the sum of the van der Waals radii (3.5 Å) of I–O.[16] Such secondary bonding interactions are well precedented in polycoordinate iodine chemistry.[8,15] A similar interaction was reported by Martin and coworkers[17] in the 10-I-3 iodinane **7** with an I---O intermolecular bond length of about 3.0 Å. It is interesting to speculate if the considerably shorter I---O distances in **6** vs **7** are due to the different nucleophilicities of the oxygens involved and the electrophilicities of the respective iodine centers as well as the similarity of the trans substituents in **6**.



7

Treatment of **5** in $CDCl_3$ with $NaOD/D_2O$ results in *complete* exchange of the vinylic proton as evidenced by the infrared shift of the C=CH group (from 3080 to 2300 cm^{-1} for the stretching mode and 795 to 564 cm^{-1} for the out-of-plane vibration) and the complete disappearance of the 5.91 ppm vinylic proton signal in the NMR. The deuteriated isomer of **5** is recovered quantitatively. This represents prima facie evidence[18] for the intermediacy of an alkylidenecarbene–iodonium ylide (**2**) with a finite lifetime.

In summary, we report the X-ray structure of a vinyliodinane species with 12-I-4 structural features and present evidence for an alkylidenecarbene–iodonium ylide (**2**). Attempts to isolate a stable ylide **2** as well as further work in this area are underway.

Acknowledgment. This work was supported by the NCI of the NIH (Grant RO1CA16903-11).

Supplementary Material Available: A complete description of the X-ray structure of **6** and tables of positional and thermal parameters (14 pages). Ordering information is given on any current masthead page.

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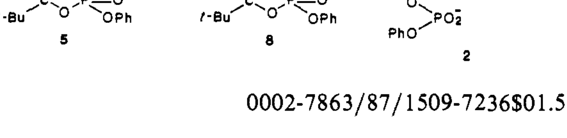
[18] A referee pointed out that a structure such as **8** can account for the results of the base exchange and cannot be ruled out on the basis of our evidence. This is correct, but **8** may be looked upon as a cyclic, closed version of the postulated ylide. Calculations and experiments are under way to distinguish between **8** and **2**.



Nature of the Tin–Tin Double Bond As Studied by Solid-State and Solution Nuclear Magnetic Resonance

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Received May 18, 1987

During the past 10 years interest in multiple bonding between heavier elements of the main group has rapidly increased as more and more examples have been synthesized and characterized.[1] One of the most interesting of these species is the dimer, **1**, of bis[bis(trimethylsilyl)methyl]tin, **2**, the first compound[2] known to formally contain a Sn=Sn double bond. Despite much work[3-5] relatively little is known about the nature of the Sn=Sn bond in **1** or its thermochromic behavior. In this paper we report NMR results that are consistent with the Sn=Sn bond in **1** being a very weak dative interaction and demonstrate that the monomer and dimer exist in equilibrium in solution.

Compound **1** was prepared[4] by standard Schlenk line techniques, and the authenticity of the sample was confirmed by X-ray crystallography.[5] Figure 1A depicts the room temperature ^{119}Sn CPMAS spectrum of **1**, giving an isotropic shift of 692 ppm downfield from tetramethyltin which moves upfield to 613 ppm at 77 K. This spectrum and all subsequent solid-state spectra were collected by using a variable-temperature CPMAS probe head that spins short sealed 5-mm NMR tubes.[6] Such sample cells were necessary due to the extreme sensitivity of **1** to air and moisture. Analysis of the spinning sideband intensities[7] gives the principal values of the chemical shielding tensor as $\sigma_{11} = 1600$, $\sigma_{22} = 400$, and $\sigma_{33} = 100 \pm 20$ ppm. This anisotropy is an order of magnitude larger than those observed for several tin(IV) compounds.[8] Satellites are observed on each line in the CPMAS spectrum due to the 1340 ± 10 Hz scalar coupling to ^{117}Sn. Satellites from coupling to both ^{119}Sn and ^{117}Sn are also clearly observed in single-crystal CP spectra, where the splittings are the sum of the anisotropic direct and indirect (*J*) dipolar couplings.[9] The latter are quite anisotropic as the splittings at some orientations are over 4 times as large as can be accounted for by direct dipolar coupling alone.[10] The ^{13}C CPMAS spectrum at room temperature displays a single line for the methine carbon with satellites due to coupling with both ^{119}Sn and ^{117}Sn. Beginning at ~220 K this resonance splits into three lines which continue to shift smoothly apart down to ~100 K (Figure 2B). This behavior is most easily explained by a conformational equilibrium in the solid that is slowed upon cooling.

Attempts to observe ^{119}Sn spectra in solution at room temperature failed but two signals were observed at 165 K in either ether or toluene at 740 and 725 ppm (Figure 1B). Upon warming, these resonances broaden and shift to lower field, finally disappearing into the base line at ~225 K. Assignment of these peaks on the basis of the ^{119}Sn shifts alone is not possible as no rationale has yet emerged for the interpretation of tin(II) ^{119}Sn shifts even though they span over 4000 ppm.[11] While the shifts are close

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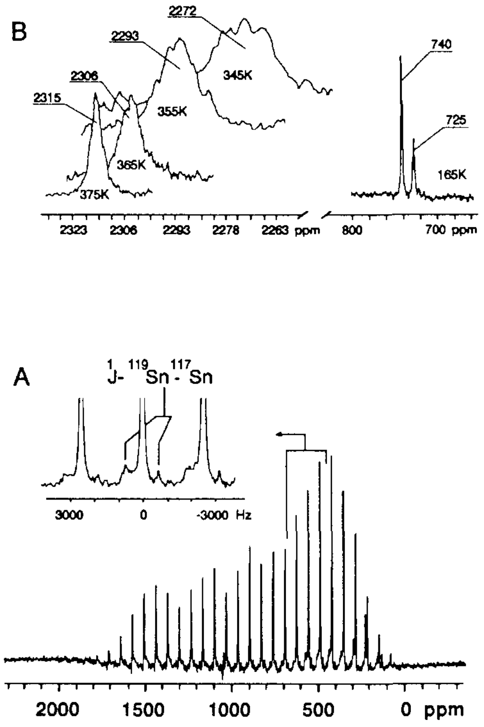

Figure 1. (A) ^{119}Sn CPMAS room temperature spectrum of **1** at 2.35 T. Satellites are observed from coupling to ^{117}Sn as shown in the inset. (B) Temperature dependence for the ^{119}Sn solution spectra at the indicated temperatures in a solution consisting of 19 mg of **1** in 1.98 mL of toluene. At high temperatures only the monomer is observed while at low temperatures two lines for the dimeric species are observed. The temperature-dependent changes in all spectra are fully reversible and have been reproduced by using several different samples and field strengths.

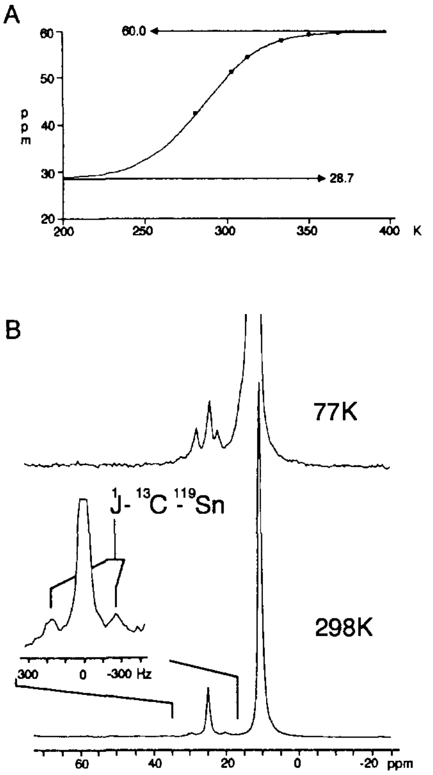

Figure 2. (A) Temperature dependence of the ^{13}C methine shift for the sample used in Figure 1B. The solid line is calculated: (●) marks the experimental data points. (B) Room temperature and 77 K ^{13}C CPMAS spectra of **1**. The inset depicts the satellites due to the 380 ± 5 Hz scalar coupling to both ^{119}Sn and ^{117}Sn. The same coupling is observed in both the solid-state and the solution ^{13}C spectra. The 28.7 ppm dimer shift in solution is in good agreement with the 26 ppm value measured in the solid at room temperature.

to that for both **1** in the solid and a stannaphosphene[12] (658 ppm), they are also close to that for the bis[bis(trimethylsilyl)amide]tin monomer[13] (776 ppm) and quite different from that for tetrakis(2,4,6-triisopropylphenyl)distannene[14] (427 ppm). The resolution and signal to noise of the solution ^{119}Sn spectra have unfortunately proven insufficient for observation of ^{117}Sn satellites.

The assignment of the low-temperature solution ^{119}Sn signals to dimers is made possible by the temperature dependence of the solution ^{13}C shift for the methine carbons (Figure 2A). These data can only be fitted[15] if a rapid monomer $\rightleftharpoons$ dimer equilibrium is assumed. The fit gives a solution ^{13}C dimer methine shift of 28.7 ppm and a monomer methine shift of 60.0 ppm and yields both the ΔH (12.8 kcal/mol) and the ΔS (33 eu) for the dissociation of **1**. From these numbers it was reasoned that the equilibrium could be shifted far enough over to the monomer at sufficiently high temperatures and low concentrations that the ^{119}Sn spectrum for **2** should also be observable. This was confirmed by the observation of a single broad line in dilute samples at 345 K which shifted to lower field and narrowed further as the temperature was raised (Figure 1B). The temperature dependence of the ^{119}Sn shift can be fitted with the same ΔH and ΔS derived from the ^{13}C data. This fit places the ^{119}Sn shift for the monomer at 2328 ppm and in conjunction with the solid-state shift confirms that the low-temperature ^{119}Sn solution resonances are indeed dimers, presumably different conformers.

The small ΔH for dissociation and the small value of ^{1}J(^{119}Sn–^{117}Sn) imply that the Sn=Sn bond in the dimer is exceptionally weak and not a covalent bond in the usual sense, in agreement with recent calculations.[5] Since the bond strength measured here is at least a factor of 2 less than that for a typical Sn—Sn bond,[17] the zwitterionic single-bond description of this molecule is probably inaccurate. However the double dative bond[3] as first proposed by Lappert, in which the lone pair on each monomer interacts with the empty p_z orbital on the other, is wholly consistent with these data. Fermi contact through such bonds would be expected to be small, which is in line with the relatively small[11c] ^{1}J(^{119}Sn–^{117}Sn). The fact that ^{1}J(^{13}C–^{119}Sn) is the same in both monomer and dimer indicates that the C—Sn bond order is essentially unchanged upon complexation, which is also consistent with this picture of the bonding. The Sn=Sn bond in **1** is then in fact not a double bond at all in the sense that C=C, Si=Si, and P=P bonds[1] are. It has been postulated that a monomer–dimer equilibrium in the solid state or a thermally accessible singlet state is responsible for the thermochromic[16] behavior of **1**. While the data here are not inconsistent with these models, the temperature dependence of the ^{13}C CPMAS spectrum suggests that the thermochromism may be conformational in origin. Whether the thermochromism is related to the conformation is an open question; however, thermochromism due to temperature-dependent conformational changes has been observed in polysilane polymers[18] and accounted for theoretically.[19] Ad-

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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**.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. CHE-8517584 and by a Grant for Newly Appointed Young Faculty in Chemistry from the Camille and Henry Dreyfus Foundation Inc.

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Deltic Acid, a Novel Compound

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Received June 8, 1987

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]

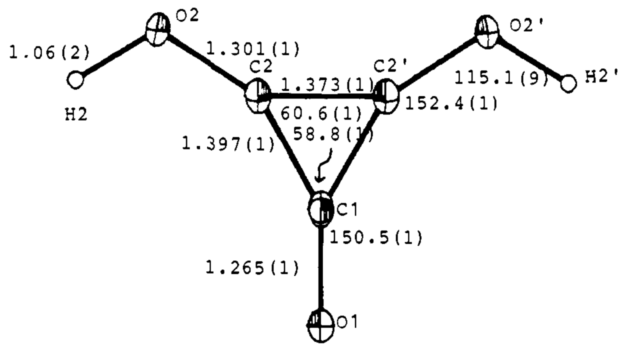

Figure 1. The deltic acid molecule with atom nomenclature: bond lengths (Å), left, and angles (deg), right. Estimated standard deviations in parenthesis.

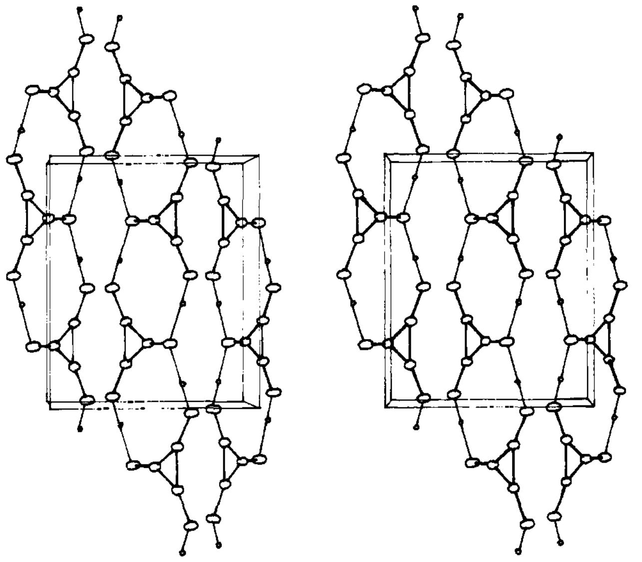

Figure 2. Stereo view of the unit cell.

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 Lautiê 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; $R = 0.034$, $R_w = 0.042$, $S = 2.26$.