

Solution and Solid-State Structures of Di-*n*-butyltin 3-Thiopropionate. X-ray Crystal Structure Determination of the Cyclic Hexamer

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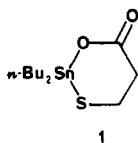
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Received May 15, 1987

Molecular weight and ^{13}C and ^{119}Sn NMR data for di-*n*-butyltin 3-thiopropionate indicate that monomer and at least two oligomers are in equilibrium in solution. The ^{119}Sn chemical shift and tin-carbon coupling constants indicate that the associative interaction gives rise to five-coordinate tin. Complicated concentration and temperature effects on the ^{119}Sn NMR spectra are rationalized by postulating the existence of a third oligomeric form at high concentration; solution viscosity measurements suggest that this species may be a linear polymer. Two crystalline modifications (monoclinic and rhombohedral) of the title compound have been identified. Full structural analysis of the monoclinic modification reveal the presence in the unit cell of two crystallographically independent cyclic hexamers in which the carboxylate group bridges between tin atoms [monomer formula $\text{C}_{11}\text{H}_{22}\text{SnO}_2\text{S}$; $a = 19.203$ (7) Å, $b = 18.269$ (10) Å, $c = 25.365$ (12) Å; $\beta = 90.70$ (3)°; refinement gave $R = 0.050$ and $R_w = 0.054$; space group $P2_1/c$, $Z = 24$]. Partial analysis of the rhombohedral form suggests pentamers of di-*n*-butyltin 3-thiopropionate.

Introduction

Interest in di-*n*-butyltin 3-thiopropionate (1) and other diorganotin mercaptides dates from the early 1950s, when they were shown to be excellent thermal and photochemical stabilizers for PVC.¹ Little is known, however, about



the solid-state and solution structures of diorganotin compounds bearing thio-substituted carboxylate ligands. Molecular weight determinations on several α - and β -thio-substituted carboxylate diorganotin complexes have indicated monomeric structures in solution,² while other studies have indicated possible polymeric compositions.³ In this paper solution and solid-state studies are described which reveal that 1 can exist in either oligomeric or monomeric form in solution, depending on temperature and concentration, and that it crystallizes as a cyclic hexamer.

Results

Vapor-phase osmometry (VPO) results obtained on a recrystallized sample of 1 over the concentration range 0.04–0.12 M in three solvents are given in Table I. At elevated temperature in either dimethylformamide or toluene, a molecular weight close to that for the monomer (mol wt 337.0) was found. At lower temperatures in chloroform and toluene, the empirical molecular weights require the presence of one or more oligomers averaging four or more repeating units. The equilibrium constant for the oligomerization appears to be somewhat solvent dependent, greater oligomerization being observed in chloroform at 45 °C than in toluene at 37 °C.

Solution ^{13}C and ^{119}Sn NMR results on 1 in chloroform and toluene at different temperatures and concentrations are given in Table II. ^{119}Sn NMR indicates the presence of a single predominant form of 1 in solution (–93 ppm) at low temperature and concentration. At modestly ele-

Table I. Vapor-Phase Osmometry Molecular Weight Data for Di-*n*-Butyltin 3-Thiopropionate

solvent	temp, °C	mol wt	calcd av oligomer size
chloroform	45	1220	3.6
dimethylformamide	90	376	1.1
toluene	27	1553	4.6
	37	1060	3.1
	60	345	1.0

Table II. Solution ^{13}C and ^{119}Sn NMR Data for Di-*n*-Butyltin 3-Thiopropionate

solv	concn, M	temp, °C	^{119}Sn chem shift, ppm (rel areas, %)	$J(^{119}\text{Sn}, ^{13}\text{C})$, Hz
CDCl_3	0.1	27	–92.5 (≥ 95)	563.2
	0.5	24	–92.5 (95), –95.6 (5)	563.6
	0.5	60	–90.1 (59), –96.2 (41)	561.7
toluene- d_6	0.1	24	–93.1 (80), –96.9 (20)	
	1.0	24	–93.1 (16), –97.5 (84)	
	1.0	44	–92.1 (11), –97.5 (89)	
	1.0	60	–91.6 (6), –97.6 (94)	

ated temperature or higher concentrations, a second resonance appears between about –95 and –98 ppm. Under no conditions did the resonances at –93 and –95 to –98 ppm show evidence of interconversion on the NMR time scale; qualitative observations suggest that equilibration of the tin species giving rise to the two resonances occurs on a scale of minutes. The upfield resonance (line width = ca. 60 Hz) was always somewhat broader than the downfield one (line width = ca. 10 Hz).

An X-ray diffraction analysis was carried out on crystals of 1 obtained from acetone solution (mp 130–135 °C). Two crystallographically distinct, though structurally similar, cyclic hexamers of 1 reside in the monoclinic crystal (Tables III and IV, Figure 1). Symmetry reduces each hexamer to three unique monomeric units in which one terminal methyl group is disordered by a bond rotation. In view of the NMR and VPO evidence that at least two

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† Contribution no. 4305.

Table III. Positional Parameters and Their Estimated Standard Deviations for Cyclic, Hexameric 1

atom	x	y	z	B, Å ²	atom	x	y	z	B, Å ²
Sn1	0.16958 (6)	-0.18683 (6)	0.09965 (3)	4.92 (2)	C3F	0.0409 (8)	0.0942 (8)	0.2317 (6)	6.1 (4)
Sn2	0.18814 (5)	-0.14582 (5)	-0.11062 (4)	4.54 (2)	C3G	0.1004 (9)	0.1494 (9)	0.2246 (7)	7.3 (4)*
Sn3	-0.02975 (5)	-0.05328 (5)	0.20726 (3)	4.35 (2)	C3H	0.088 (1)	0.221 (1)	0.2538 (7)	8.7 (5)*
Sn4	0.71570 (6)	0.69216 (6)	-0.01548 (4)	5.60 (3)	C4A	0.3931 (9)	0.281 (1)	0.0178 (7)	9.5 (6)
Sn5	0.59452 (6)	0.65350 (6)	0.17042 (4)	5.51 (2)	C4B	0.402 (1)	0.218 (1)	0.058 (1)	13.9 (8)
Sn6	0.62130 (6)	0.53583 (6)	-0.18400 (4)	5.25 (2)	C4C	0.483 (2)	0.206 (2)	0.059 (1)	17 (1)*
S1	0.2332 (2)	-0.2597 (2)	0.1620 (1)	6.3 (1)	C4D	0.489 (2)	0.137 (2)	0.086 (1)	20 (1)*
S2	0.2749 (2)	-0.2315 (2)	-0.1383 (1)	6.0 (1)	C4E	0.247 (1)	0.411 (1)	-0.0117 (8)	9.3 (6)
S3	-0.0767 (2)	-0.0645 (2)	0.2937 (2)	6.5 (1)	C4F	0.185 (1)	0.436 (1)	0.0193 (9)	12.9 (8)
S4	0.7986 (3)	0.7738 (3)	-0.0521 (2)	10.3 (1)	C4G	0.159 (2)	0.514 (2)	-0.003 (1)	17 (1)*
S5	0.6545 (2)	0.7319 (3)	0.2310 (2)	7.1 (1)	C4H	0.146 (2)	0.566 (2)	0.033 (1)	21 (1)*
S6	0.6597 (2)	0.5199 (3)	-0.2725 (2)	6.9 (1)	C5A	0.5084 (8)	0.6964 (9)	0.1253 (6)	7.3 (4)
O10	0.1004 (5)	-0.1445 (5)	0.1650 (3)	4.9 (2)	C5B	0.5094 (8)	0.779 (1)	0.1218 (7)	7.6 (5)
O11	0.0394 (5)	-0.1404 (5)	0.2371 (3)	5.3 (2)	C5C	0.440 (1)	0.803 (1)	0.0908 (8)	9.3 (5)*
O20	0.2033 (5)	-0.1856 (5)	-0.0266 (3)	5.4 (2)	C5D	0.437 (1)	0.885 (1)	0.089 (1)	13.6 (8)*
O21	0.2463 (5)	-0.2334 (6)	0.0469 (4)	7.6 (3)	C5E	0.6337 (9)	0.546 (1)	0.1600 (8)	8.4 (5)
O30	-0.1121 (5)	0.0350 (5)	0.1893 (3)	4.9 (2)	C5F	0.712 (1)	0.5433 (9)	0.1702 (7)	8.1 (5)
O31	0.1873 (5)	-0.1227 (5)	-0.1958 (3)	5.7 (2)	C5G	0.741 (1)	0.465 (1)	0.1656 (9)	10.8 (6)*
O40	0.6985 (5)	0.6422 (5)	-0.0979 (3)	6.0 (2)	C5H	0.822 (1)	0.456 (1)	0.1763 (9)	11.4 (6)*
O41	0.7024 (5)	0.6198 (5)	-0.1819 (3)	5.6 (2)	C6A	0.663 (1)	0.4656 (8)	-0.1249 (6)	7.4 (5)
O50	0.6652 (5)	0.6927 (5)	0.1046 (4)	5.9 (2)	C6B	0.603 (1)	0.473 (1)	-0.0733 (7)	9.3 (5)
O51	0.7420 (6)	0.7495 (7)	0.0572 (4)	10.7 (3)	C6C	0.619 (1)	0.421 (1)	-0.0378 (9)	12.1 (7)*
O60	0.5389 (5)	0.4465 (6)	-0.1996 (4)	6.8 (3)	C6D	0.573 (1)	0.429 (1)	0.0103 (8)	9.2 (5)*
O61	0.5342 (5)	0.6278 (6)	0.2398 (4)	7.7 (3)	C6E	0.5397 (9)	0.611 (1)	-0.1684 (7)	8.5 (5)
C1A	0.2007 (9)	-0.0760 (9)	0.0886 (6)	7.3 (4)	C6F	0.4947 (9)	0.624 (1)	-0.2201 (8)	9.3 (6)
C1B	0.249 (1)	-0.0524 (9)	0.1345 (7)	8.1 (5)	C6G	0.438 (1)	0.680 (1)	-0.2047 (9)	11.1 (6)*
C1C	0.273 (1)	0.025 (1)	0.1271 (9)	10.8 (6)*	C6H	0.395 (1)	0.695 (1)	-0.2549 (9)	11.6 (6)*
C1D	0.322 (1)	0.050 (1)	0.172 (1)	12.2 (7)*	C10	0.0886 (6)	-0.1660 (7)	0.2103 (5)	4.4 (3)
C1E	0.0810 (8)	-0.2388 (8)	0.0638 (6)	6.4 (4)	C11	0.1308 (7)	-0.2270 (8)	0.2381 (5)	5.5 (3)
C1F	0.045 (1)	-0.293 (1)	0.0995 (7)	8.6 (5)	C12	0.2071 (8)	-0.2232 (8)	0.2259 (5)	5.6 (4)
C1G	-0.022 (1)	-0.330 (1)	0.0723 (8)	10.3 (6)*	C20	0.2477 (8)	-0.2245 (8)	-0.0030 (5)	6.3 (4)
C1H	-0.056 (1)	-0.388 (1)	0.106 (1)	13.4 (8)*	C21	0.3079 (9)	-0.259 (1)	-0.0336 (6)	9.2 (5)
C2A	0.0813 (9)	-0.1839 (9)	-0.1060 (7)	7.9 (5)	C22	0.291 (1)	-0.289 (1)	-0.0825 (6)	11.6 (5)
C2B	0.0817 (9)	-0.268 (1)	-0.0994 (6)	8.7 (5)	C30	-0.1512 (7)	0.0719 (7)	0.2158 (5)	4.2 (3)
C2C	0.008 (1)	-0.295 (1)	-0.0981 (9)	11.4 (6)*	C31	-0.1600 (8)	0.0620 (8)	0.2735 (5)	6.2 (4)
C2D	0.007 (1)	-0.379 (1)	-0.0836 (9)	10.7 (6)*	C32	-0.158 (1)	-0.014 (1)	0.2908 (7)	10.0 (5)
C2E	0.2253 (8)	-0.0403 (8)	-0.0885 (7)	7.4 (4)	C40	0.7229 (7)	0.6552 (7)	-0.1415 (5)	4.5 (3)
C2F	0.298 (1)	-0.0446 (9)	-0.0637 (7)	8.3 (5)	C41	0.7776 (8)	0.7126 (8)	-0.1523 (6)	6.4 (4)
C2G	0.321 (1)	0.036 (2)	-0.047 (1)	13.9 (8)*	C42B	0.829 (1)	0.722 (2)	-0.111 (1)	6.8 (8)
C2H	0.341 (3)	0.071 (3)	-0.076 (2)	16 (2)*	C42A	0.771 (2)	0.780 (2)	-0.121 (1)	9.2 (9)
C2I	0.390 (3)	0.034 (3)	-0.033 (2)	13 (1)*	C50	0.7122 (9)	0.737 (1)	0.1008 (6)	7.9 (5)
C3A	-0.0738 (8)	-0.1105 (7)	0.1415 (5)	5.2 (3)	C51	0.742 (1)	0.778 (1)	0.1482 (7)	14.7 (6)
C3B	-0.0547 (7)	-0.0750 (8)	0.0901 (5)	5.1 (3)	C52	0.709 (1)	0.786 (1)	0.1922 (6)	9.9 (5)
C3C	-0.0925 (8)	-0.1127 (9)	0.0436 (6)	6.3 (4)*	C60	0.5216 (8)	0.4104 (8)	-0.2390 (7)	6.8 (4)
C3D	-0.0711 (9)	-0.077 (1)	-0.0094 (7)	8.2 (5)*	C61	0.5621 (9)	0.407 (1)	-0.2893 (6)	9.8 (5)
C3E	0.0509 (8)	0.0270 (7)	0.1968 (6)	5.7 (4)	C62	0.6387 (9)	0.421 (1)	-0.2811 (6)	9.0 (5)

* Thermal parameters with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(\frac{1}{3})[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

oligomers of 1 exist in solution and that they interconvert readily, attempts were made to isolate other crystalline forms. Whereas recrystallization of 1 from mixtures of toluene with polar solvents gave monoclinic 1, a second crystalline modification (rhombohedral, mp 80 °C) was isolated from cyclohexane solution. Partial analysis of the X-ray data for rhombohedral 1 indicated the presence of either pentamers or, possibly, decamers of 1. A full structure analysis of this modification was not carried out.

The solid-state ¹³C NMR spectrum of monomeric 1 was determined for a polycrystalline sample. As expected from the crystal structure and previous solid-state NMR studies,⁴ the many crystallographically nonequivalent carbons in the cyclic hexamer gave rise to a larger number of resonances for the solid sample than were found in solution. The tin-carbon coupling constants were not resolved in the spectrum of the solid.

Discussion

Solid-State Structure of 1. The X-ray structure determination of monoclinic 1 reveals cyclic hexamers held

together by bridging carboxylate groups. The bonding at each tin is close to trigonal bipyramidal with the *n*-butyl groups and sulfur lying in the equatorial plane (average $\angle\text{C-Sn-C} = 123.5^\circ$). The apical oxygens make an average angle of 171.1° with tin. The carboxylates bond to tin in a highly symmetric fashion (the average difference between Sn-O bonds for each tin is 0.10 Å) and the C-O distances within each carboxylate moiety do not differ significantly, indicating substantial delocalization of the CO₂ π -electron density.⁵ Carboxylate bridging is frequently observed for triorganotin carboxylates, many of which exist as linear polymers in the solid state.⁶ The Sn-O bonds in cyclic, hexameric 1 range from 2.17 to 2.31 Å and are significantly shorter than those reported for any of the polymeric triorganotin carboxylates yet studied.⁵

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Table IV. Selected Bond Distances (Å) and Angles (deg) for the Two Crystallographically Distinct Molecules of Di-*n*-Butyltin 3-Thioproionate^a

atom 1	atom 2	dist	atom 1	atom 2	dist
Sn1	S1	2.391 (5)	Sn5	O50	2.279 (9)
Sn1	O10	2.274 (8)	Sn5	O61	2.18 (2)
Sn1	O21	2.18 (2)	Sn5	C5A	2.15 (2)
Sn1	C1A	2.14 (2)	Sn5	C5E	2.12 (2)
Sn1	C1E	2.15 (2)	Sn6	S6	2.388 (4)
Sn2	S2	2.398 (4)	Sn6	O41	2.186 (9)
Sn2	O20	2.268 (8)	Sn6	O60	2.31 (1)
Sn2	O31	2.201 (8)	Sn6	C6A	2.13 (2)
Sn2	C2A	2.17 (2)	Sn6	C6E	2.12 (2)
Sn2	C2E	2.13 (2)	O10	C10	1.24 (1)
Sn3	S3	2.389 (4)	O11	C10	1.27 (2)
Sn3	O11	2.201 (9)	O20	C20	1.26 (2)
Sn3	O30	2.300 (9)	O21	C20	1.28 (2)
Sn3	C3A	2.14 (1)	O30	C30	1.22 (1)
Sn3	C3E	2.15 (1)	O31	C30	1.26 (2)
Sn4	S4	2.379 (5)	O40	C40	1.24 (2)
Sn4	O40	2.302 (9)	O41	C40	1.27 (2)
Sn4	O51	2.17 (1)	O50	C50	1.22 (3)
Sn4	C4A	2.15 (2)	O51	C50	1.27 (2)
Sn4	C4E	2.13 (2)	O60	C60	1.24 (2)
Sn5	S5	2.387 (4)	O61	C60	1.28 (2)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
S1	Sn1	O10	90.4 (2)	S4	Sn4	O40	89.0 (3)
S1	Sn1	O21	81.1 (3)	S4	Sn4	O51	83.1 (3)
S1	Sn1	C1A	118.3 (5)	S4	Sn4	C4A	119.9 (6)
S1	Sn1	C1E	115.5 (4)	S4	Sn4	C4E	117.5 (5)
O10	Sn1	O21	171.1 (3)	O40	Sn4	O51	172.1 (4)
O10	Sn1	C1A	86.6 (5)	O40	Sn4	C4A	86.6 (6)
O10	Sn1	C1E	89.5 (5)	O40	Sn4	C4E	89.2 (6)
O21	Sn1	C1A	95.7 (5)	O51	Sn4	C4A	97.2 (7)
O21	Sn1	C1E	96.2 (5)	O51	Sn4	C4E	94.6 (6)
C1A	Sn1	C1E	126.1 (7)	C4A	Sn4	C4E	122.3 (8)
S2	Sn2	O20	89.1 (2)	S5	Sn5	O50	89.8 (3)
S2	Sn2	O31	80.5 (3)	S5	Sn5	O61	82.3 (4)
S2	Sn2	C2A	117.9 (5)	S5	Sn5	C5A	119.1 (5)
S2	Sn2	C2E	115.9 (4)	S5	Sn5	C5E	117.8 (6)
O20	Sn2	O31	169.6 (3)	O50	Sn5	O61	172.0 (4)
O20	Sn2	C2A	87.6 (5)	O50	Sn5	C5A	87.6 (5)
O20	Sn2	C2E	90.2 (6)	O50	Sn5	C5E	89.1 (6)
O31	Sn2	C2A	96.8 (5)	O61	Sn5	C5A	95.5 (6)
O31	Sn2	C2E	94.7 (6)	O61	Sn5	C5E	95.5 (7)
C2A	Sn2	C2E	126.1 (6)	C5A	Sn5	C5E	122.9 (7)
S3	Sn3	O11	81.7 (2)	S6	Sn6	O41	83.1 (2)
S3	Sn3	O30	88.6 (2)	S6	Sn6	O60	88.3 (3)
S3	Sn3	C3A	121.6 (4)	S6	Sn6	C6A	118.0 (4)
S3	Sn3	C3E	117.0 (4)	S6	Sn6	C6E	119.4 (5)
O11	Sn3	O30	170.3 (4)	O41	Sn6	O60	171.4 (3)
O11	Sn3	C3A	98.4 (4)	O41	Sn6	C6A	98.1 (5)
O11	Sn3	C3E	95.9 (4)	O41	Sn6	C6E	93.9 (5)
O30	Sn3	C3A	85.6 (4)	O60	Sn6	C6A	87.1 (5)
O30	Sn3	C3E	89.5 (4)	O60	Sn6	C6E	89.1 (5)
C3A	Sn3	C3E	121.1 (5)	C6A	Sn6	C6E	122.3 (7)

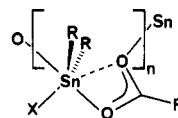
^a See Figure 1 for atom numbering scheme. Uncertainty in last significant figure in parentheses.

The ring can be viewed as arising from the association of cyclic monomers through interaction of the carboxylate oxygen of one cyclic monomer with a neighboring tin atom. Such a description is supported by the observation by VPO that monomeric, cyclic **1** exists in dilute solution at elevated temperature. However, the fact that the intermonomer Sn–O bonds are 0.10 Å shorter on average than the intramonomer ones suggests the alternate view of the hexamer as a large (36-membered) macrocycle reinforced by additional intramonomer Sn–carboxylate interactions.

The hexamer ring is quite flat; the greatest distance from the plane formed by the tin atoms of molecule **1** (Sn1, Sn2, Sn3, Sn1', Sn2', and Sn3') is only 0.438 Å. The corresponding deviation (0.206 Å) for the second hexamer is smaller yet. The angle between the planes of tin atoms of molecules **1** and **2** is 92.5°.

It has been suggested recently that for some di- and triorganotin carboxylates one of the carboxylate oxygens

can bridge between adjacent tin atoms in a bidentate fashion, giving rise to hexacoordinate tin as shown below.



This suggestion seems reasonable for Me₂Sn(Cl)O₂CMe,¹⁰ where the third Sn–O interaction occurs over a distance of 2.782 (7) Å. The comparable, potentially bridging Sn–O distances are substantially longer for the less Lewis acidic triorganotin carboxylates. Nevertheless, Molloy and co-workers¹¹ have suggested that such an interaction over

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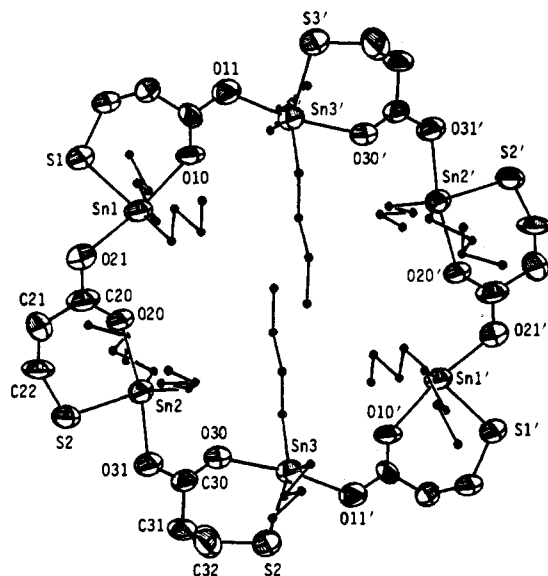


Figure 1. View of molecule 1 of $n\text{-Bu}_2\text{SnSCH}_2\text{CH}_2\text{CO}_2$ showing partial atom numbering scheme [primes (') indicate symmetry-related atoms]. *n*-Butyl carbons numbered same as tin to which they are bonded, with atoms of each *n*-butyl group lettered A to D and E to F from the $\alpha\text{-CH}_2$ outward to the methyl terminus. Thus on Sn2 the *n*-butyls are labeled C2(A-D) and C2(E-F). Molecule 2 is labeled Sn4 to Sn6 and uses the same numbering scheme.

3.206 (3) Å is energetically significant for $\text{Ph}_3\text{SnO}_2\text{CMe}$, largely on the evidence of the expanded C-Sn-C angle [135.2 (1)°]. For 1, the corresponding bridging Sn-O distances range from 3.19 to 3.28 Å. While the tin atoms in monoclinic 1 (Figure 1) are nearly coplanar with three oxygens and sulfur and the overall configuration about tin resembles the skew octahedral geometry commonly encountered for diorganotin bis(chelates),¹² the modest deviation of the C-Sn-C angles from 120° does not strongly encourage such a structural interpretation.¹³ More generally, it should be noted that it is extremely difficult to gauge the energetic significance of possible interactions between two atoms over distances approaching the sum of their van der Waals radii (for Sn and O, 3.68 Å).¹⁴ This type of problem has arisen elsewhere in organotin chemistry.¹⁵

Solution Structure of 1. Comparison of the range of ^{119}Sn chemical shifts observed for 1, -90 to -98 ppm, with those observed for reasonable five-coordinate analogues 2 and 3 (these are dimers in solution and have ^{119}Sn



chemical shifts of -32 and -164 ppm, respectively¹⁶) suggests that tin is five-coordinate in the oligomeric forms of 1. Monomeric 1 was not detected by ^{119}Sn NMR under the conditions used. Five-coordinate tin is also suggested by the large tin-carbon coupling constant, $^1J(^{119}\text{Sn},^{13}\text{C})$,

observed in ^{13}C NMR spectra of 1 in chloroform, 563 Hz.¹⁷ An empirical relationship between $^1J(^{119}\text{Sn},^{13}\text{C})$ and the C-Sn-C angle has been revealed by recent solid-state NMR studies of a wide variety of structurally characterized methyltin compounds.¹⁸ From more qualitative solution NMR studies a second correlation has been derived recently for di-*n*-butyltin compounds.¹⁹ From $^1J(^{119}\text{Sn},^{13}\text{C})$ for 1 the C-Sn-C angle in solution is estimated to be about $131 \pm 10^\circ$, which compares reasonably well with the angles found for the cyclic hexamer by X-ray ($121.1\text{--}126.1^\circ$, average = 123.5°). Strangely, at elevated temperature where a mixture of two oligomers of 1 is present, the butyl carbons α and β to tin give rise to only single ^{13}C resonances and $^1J(^{119}\text{Sn},^{13}\text{C})$ values (all other carbon resonances are doubled). This seems to indicate an extremely similar local environment at tin in the two different oligomeric forms of 1 present in the solution. Comparison of the ^{119}Sn NMR data for 0.1 M toluene and chloroform solutions of 1 suggests, as does the VPO data, that solvent has a modest influence on the equilibrium between oligomeric forms of 1.

VPO results indicate that the relative amount of monomeric 1 in solution increases with increasing temperature; this is in accord with expectations that monomer formation is accompanied by a substantial increase in translational entropy. The concentration and temperature dependence of the ^{119}Sn NMR data, however, pose an apparent contradiction: While increasing concentration of 1 should favor formation of fewer species in solution (larger cyclic oligomers or polymer) and temperature increases should always drive the system toward a larger number of species (smaller oligomers or monomers), both temperature and concentration increases produce a larger ^{119}Sn resonance between -95 and -98 ppm (Table II). One possible explanation for the observed behavior is that the oligomer with ^{119}Sn chemical shift from -90 to -93 ppm is transformed at higher concentrations to a larger oligomer (or polymer) and at elevated temperature to a third (smaller) oligomer both of which coincidentally have ^{119}Sn chemical shifts between -95 and -98 ppm. Concentrated solutions of 1 are quite viscous (a 1 M solution in toluene was found to have a viscosity of 5.5×10^3 centistokes), an observation which is consistent with, but does not require, the formation of polymeric 1.

The NMR and VPO results described above clearly show that 1 can exist in monomeric and two or more oligomeric forms in solution and that the tin atoms in the oligomers are five-coordinate. The isolation of two oligomeric crystalline forms of 1 strongly reinforces the suggestion that more than one cyclic oligomer can exist in solution. The possible existence of yet a third crystalline form is suggested by the melting point of 119.4 °C reported in the literature.²⁰

The results for 1 are reminiscent of earlier observations made on $\text{Me}_3\text{SnO}_2\text{CMe}$ and $\text{Me}_3\text{SnO}_2\text{CH}$. Simon and Graham²¹ found that the insoluble, presumably polymeric, crystalline form of these compounds could be converted to a soluble form by heating to 100 °C in cyclohexane solution. Spectroscopic investigations of the soluble forms

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in solution indicated that monomer exists in equilibrium with oligomeric forms that were assigned a cyclic structure, depending on concentration and temperature. The crystalline soluble forms of these compounds have distinctly different melting points than the insoluble forms, and it was hypothesized that the soluble forms exist as cyclic oligomers in the solid state. A later X-ray study of $\text{Me}_3\text{SnO}_2\text{CMe}^{22}$ revealed a linear polymeric structure, although it is not clear from that report whether the soluble or insoluble form had been examined.

The present work provides the first direct evidence for the existence of cyclic oligomers of organotin carboxylates in the solid state. The facile interconversion of monomeric **1** with various oligomeric forms over a narrow range of concentration and temperature indicates that the free energy of these different structural forms is very closely balanced and that the enthalpic gain from forming a bridging carboxylate bond is approximately equal to the loss of translational entropy in these systems. The complicated dynamics of **1** in solution frustrated our carrying out an evaluation of the enthalpy of the bridging Sn-carboxylate interaction. Similar solution studies on simpler systems may allow this important thermodynamic parameter to be evaluated.

Experimental Section

Compound **1** was obtained from Pfaltz and Bauer and recrystallized from hot acetone to give clear, colorless hexagonal plates [mp 130–135 °C (lit.²⁰ mp 119.4 °C)]. Elemental analyses for C, H, S, and Sn were within 0.2% of the calculated values. ^{119}Sn NMR spectra all showed ca. 5% (total) of other tin-containing compounds, even after repeated recrystallizations from acetone or toluene mixtures with diethyl ether and ethanol. The unidentified impurities had ^{119}Sn chemical shifts similar to those observed for **1** but did not participate in dynamic NMR phenomena with **1** under the conditions employed. Additional crystalline samples for X-ray analysis were obtained from cyclohexane and chloroform-acetone, toluene-diethyl ether, and toluene-ethanol mixtures. The crop of (rhombohedral) crystals from cyclohexane solution melted at 80 °C. Crystals isolated from the toluene-containing solvent mixtures were shown by X-ray to be of the monoclinic form. Crystals from chloroform-acetone were amorphous to X-ray.

Molecular weight determinations (VPO method) were performed at Galbraith Laboratories. Data for each solvent and temperature were obtained for three concentrations of solute over a twofold or greater range of concentrations (between 0.04 and 0.12 M).

NMR Spectroscopy. Solution spectra were obtained on a General Electric NT-300 spectrometer at 75 MHz for ^{13}C and 112.1 MHz for ^{119}Sn . Me_4Si (0 ppm) was employed as external reference for ^{13}C NMR spectra. The following ^{13}C resonances (and their assignments) were observed for **1** in CDCl_3 (0.1 M) at 24 °C: 13.86 (Me), 22.03 (CH_2S), 23.01 ($\alpha\text{-CH}_2$, $^1J(^{119}\text{Sn}, \text{C}) = 563.2, 539.2$ Hz), 26.69 ($\gamma\text{-CH}_2$, $^3J(^{119}\text{Sn}, \text{C}) = 102$ Hz (unresolved)), 27.79 ($\beta\text{-CH}_2$, $^2J(^{119}\text{Sn}, \text{C}) = 39$ Hz (unresolved)), 38.71 ($^{13}\text{CH}_2\text{CO}_2$), 181.77 ppm (CO_2). At 60 °C and 0.5 M in CDCl_3 , nearly equal-sized resonances were observed at 13.65 and 13.72, 22.20 and 22.30, 181.03 and 181.78 ppm. The resonance at 27.78 ppm had an unresolved shoulder, but the resonances at 23.36 and 26.59 ppm showed no evidence of broadening. ^{119}Sn spectra were referenced to Me_4Sn (0 ppm) and obtained by using a DEPT pulse sequence where the final proton pulse (θ pulse) was set between 35 and 40°. MLEV16 decoupling was used during the acquisition.

The solid-state ^{13}C (MAS) spectrum of a monoclinic sample of di-*n*-butyltin 3-thiopropionate was obtained on a Bruker CXP-300 spectrometer at 75.5 MHz. Dry nitrogen gas was used to drive MAS rates of 4.5 kHz. The Hartmann-Hann matching condition for cross-polarization (CP) was calibrated by using adamantane, and both CP (5 ms) and decoupling (40 Ms) were performed at the same proton decoupling amplitude (71 kHz).

A 4-s recycle delay was used, and the spectrum was obtained after 1000 scans. Chemical shifts were determined relative to Me_4Si by using an external sample of adamantane as reference. Major resonances were observed at chemical shift values close to those found in CHCl_3 solution. Resonances observed: 14.4 (s) 15.3, 20.4 (s), 22.9, 24.2 (sh), 27.0 (sh), 28.5, 28.9 (sh), 40.4 ppm (s = small and sh = shoulder). The carboxylate groups appeared as an approximately equivalent doublet at 181.6 and 181.9 ppm.

Crystal Structure Determinations. Carried out by Dr. R. R. Whittle, Oneida Research Services. A colorless rectangular crystal of **1** (from acetone) having approximate dimensions $0.24 \times 0.28 \times 0.45$ mm was mounted in a glass capillary. Preliminary examination and data collection were performed with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) on an Enraf-Nonius CAD4 computer-controlled κ axis diffractometer equipped with a graphite crystal, incident beam monochromator. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $10 < \theta < 14^\circ$. The monoclinic cell parameters and calculated volume are $a = 19.203$ (7) Å, $b = 18.269$ (10) Å, $c = 25.365$ (12) Å, $\beta = 90.70$ (3)°, and $V = 8898$ (12) Å³. For $Z = 24$ and $fw = 337.05$, corresponding to a monomeric formulation, the calculated density is 1.51 g/cm³. From the systematic absences $0k0$, $k = 2n + 1$, and $h0l$, and $l = 2n + 1$, the space group was determined to be $P2_1/c$ (No. 14). Data were collected at a temperature of -35 (1) °C using the ω - 2θ scan technique. The scan rate varied from 2 to 7 deg/min (in ω). Data were collected to a maximum 2θ of 42.0° and for $+h, +k, \pm l$. The θ scan width = $(1.2 + 0.140 \tan \theta)^\circ$.

A total of 10287 reflections were collected, of which 9506 were unique and not systematically absent. As a check on crystal and electronic stability three representative reflections were measured every 30 min. A linear decay correction was applied. The correction factors on I ranged from 1.000 to 1.163 with an average value of 1.072. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 18.5 cm⁻¹ for Mo $K\alpha$ radiation. No absorption correction was made. Intensities of equivalent reflections were averaged. Four reflections were rejected from the averaging process because their intensities differed significantly from the average. The agreement factors for the averaging of the 501 observed and accepted reflections were 1.9% based on intensity and 1.7% based on F_o .

The structure was solved by direct methods that revealed a total of six independent Sn atoms. This leads to two different unique hexamers that are centered about inversion centers. The remaining atoms were located in succeeding difference Fourier syntheses. Each asymmetric unit contained one disordered carbon atom. Hydrogen atoms were not included in the calculations. The structure was refined by full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)$. Unit weights were used for all observed reflections. Neutral atom scattering factors were taken from Cromer and Wagner.²³ Anomalous dispersion effects were included in F_c ; the values for f' and f'' were those of Cromer.²⁵ Only the 6470 reflections having intensities greater than 2.0 times their standard deviation were used in the refinements. The final cycle of refinement included 704 variable parameters and converged (largest parameter shift was 0.08 times its esd) with unweighted and weighted agreement factors of $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.050$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.054$. The standard deviation of an observation of unit weight was 6.57. The highest peak in the final Fourier had a height of 0.99 e/Å³ with an estimated error based on $\Delta F^{2\sigma}$ of 0.11. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $(\sin \theta) / \lambda$, and various classes of indices showed no unusual trends. All calculations were performed on a VAX-11/750 computer using SDP-PLUS.

Single-crystal X-ray diffraction data were also collected for a rhombohedral crystal of **1** obtained from cyclohexane solution. Data collected were only partially analyzed; the following cell

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constants were obtained: $a = 22.42 \text{ \AA}$, $b = 22.43 \text{ \AA}$, $c = 22.44 \text{ \AA}$, $\alpha = 99.03^\circ$; $\beta = 98.96^\circ$, $\gamma = 99.05^\circ$, and $V = 10818 \text{ \AA}^3$. With the assumption of approximately the same monomer volume as found for the hexamer, an estimate of 90 monomers per unit cell is derived from the unit cell volume. For the possible Z values of 18 or 36, $Z = 18$ indicates pentamers, or possibly decamers, of 1.

Acknowledgment. The assistance of Frederic Davidson, Rodney D. Farlee, and Robert F. Carver in obtaining

NMR spectra is gratefully acknowledged.

Registry No. 1 (hexamer), 113725-88-5; 1 (homopolymer), 73589-65-8.

Supplementary Material Available: Tables of complete structural parameters (bond lengths, bond angles, torsion angles, and least-squares planes), positional parameters, general displacement parameter expressions, and intensity data (14 pages); a listing of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

^{29}Si NMR Access to Stereochemistry of Organosilicon Compounds. 3. Vinyl Silanes

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Received October 30, 1987

^{29}Si NMR data are reported for a series of vinylic and acetylenic silanes. Chemical shifts were measured and $^{29}\text{Si}, ^1\text{H}$ coupling constants were determined by using the selective polarization transfer (SPT) technique. It was found in particular that there is a relationship between 3J and the stereochemistry of the molecules.

In a previous paper,¹ we described the first stereochemical study using ^{29}Si NMR spectroscopy and showed that this technique is capable of determining with precision the geometry of silylcyclopropyl compounds. It was found in particular that there is a Karplus-type relationship for $^3J(^{29}\text{Si}, ^1\text{H})$ coupling constants.

We now focus on the vinylsilanes, a class of compounds that is useful in organic synthesis.² Because vinylsilanes can undergo regiospecific functionalization, it appears important to be able to determine their geometric configuration.

Results and Discussion

Vinylsilanes have been the subject of intensive studies for a number of years. Publications reporting ^{29}Si NMR chemical shifts are numerous but rarely contain $^{29}\text{Si}, ^1\text{H}$ coupling constant values; if present, the latter are generally incomplete.^{3a}

Recently, Jakobsen^{3b} determined the $^{29}\text{Si}, ^1\text{H}$ coupling constants of vinyltrimethylsilane by double-resonance Hamiltonian analysis of a spectrum in which the SiMe_3 protons are selectively decoupled and concluded that it would be impossible to make such a determination without such an analysis because of the complexity of the ^{29}Si spectrum, especially when it is obtained by the SPT (selective polarization transfer) technique. Concurrently, we were studying this compound by using the SPT technique. We found the same coupling constant values and obtained a perfect simulation as shown in Figure 1.

To the best of our knowledge, a systematic study of $^{29}\text{Si}, ^1\text{H}$ coupling constants in substituted vinylsilanes as a function of stereochemistry and the substitution on silicon and carbon has not been reported. We have recorded ^{29}Si NMR spectra of 11 vinylic silanes of known stereochemistry. Complete analysis of the SPT spectra with polarization transfer from the trimethylsilyl protons, which are very easy to obtain, is possible by using a computer simulation program such as the one we have described.^{1,4} It allows the determination of all of the coupling constants (even the smallest ones) with a precision better than 0.3 Hz (cf. Figure 2). Stereochemical assignment then becomes possible from examination of 3J values. Results are given in Table I which also contains data on vinyltrimethylsilane itself and on two alkynylsilanes.

1. Chemical Shifts. Although the ^{29}Si chemical shifts of some vinylsilanes have been investigated previously,^{3,5} we have redetermined these values in order to have a uniform set of results. Because of differences in the solvents used and the operating conditions, some discrepancies between our data and literature values were observed; chemical shifts may vary within a 2 ppm range.^{3a,5,6}

We observed negative chemical shift values for all silicon atoms linked to a double bond. In compound 9, Si_b res-

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