N-Trimethyltin Aziridine, an Associated Organotin Amine

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All organotin amines in which the only nitrogen atom in the molecule is bonded to tin are monomeric.[2-3] We now report the properties of N-trimethyltin aziridine,[4] which is associated in the solid-state, solution and gas phases.

We have prepared N-trimethyltin aziridine by the transamination of trimethyl(dimethylamino) stannane with aziridine, and by the lithioamination of trimethyltin chloride or acetate, the last named being the most convenient method (45% yield). The product was previously reported from transamination as a liquid (b.pt. 53–56 °C/16 torr),[5] like its silicon[6-8] and germanium[9] analogues, but careful sublimation at room temperature on the vacuum manifold gives long, white needles, m.pt. 28.5 °C. The melting point of the corresponding dimethylamino derivative which differs in molecular weight by only two units is reported as –79 °C,[10] and to our knowledge all known trialkyltin amines are liquids at ambient temperatures,[2-3] except for the N-trialkylstannyl heterocycles containing nitrogen atoms in 1,3-positions in a conjugated ring, as is the case with the imidazole, benzimidazole, 1,2,3- and 1,2,4-triazole and benztriazoles which are well-crystallized and stable to hydrolysis as solids, with melting points above 220 °C.[11-13] The crystal stabilization arises from association by the second nitrogen atom to form a one-dimensional polymer with planar trimethyltin groups. The ^{119m}Sn Mössbauer Quadrupole Splittings (Q.S.) are in the range 2.5–3.0 mm/ s[14-15] *vs.* only 1.0 mm/s for $(CH_3)_3SnN(C_2H_5)_2$, for example.[16]

N-Trimethyltin aziridine, which exhibits a Q.S. of 2.24 mm/s, is listed in Table I together with its 2-methyl- and 2,2-dimethyl analogues and homologues in which tin is attached to cyclic amines with three to seven members. The N-piperadine derivative is known;[17] the remainder were synthesized by trans- and lithioamination. The Mössbauer data for trimethyl(dimethylamino)stannane,[17] which we have measured for the first time, are also shown. It is seen that the open-chain and cyclic derivatives with ring sizes greater than four exhibit Q.S. values of 0.8

TABLE I. Tin-119m Mössbauer Data for Organotin Aziridines, Their Derivatives and Selected Organotin Amines.[a]

	I.S.[b]	Q.S.[c]	Γ_1[b]	Γ_2[b]
$(CH_3)_3Sn-N\langle$ (aziridine)	1.21	2.24	1.15	1.15
	1.20[d]	2.35	0.84	1.17
$(CH_3)_3Sn-N\langle^{CH_3}$	1.17	1.43	1.16	1.26
$(CH_3)_3Sn-N\langle^{CH_3}_{CH_3}$	1.18	1.04	1.06	1.06
$(CH_3)_3Sn-N\langle\rangle$	1.23	1.35	1.16	1.19
$(CH_3)_3Sn-N\bigcirc$	1.24	0.91	1.12	1.02
$(CH_3)_3Sn-N\bigcirc$	1.19	0.86	0.75	1.01
$(CH_3)_3Sn-N\bigcirc$	1.19	1.05	1.25	1.04
$(CH_3)_3Sn-N(CH_3)_2$	1.29	0.81	1.02	1.02
$(CH_3)_3Sn-N(C_2H_5)_2$[e]	1.25	0.92	1.19	1.29
$(CH_3)_3Sn-N\langle \rightarrow BF_3$	1.28	3.03	1.33	1.46

[a] Recorded at 77K *vs.* a $Ba^{119m}SnO_3$ (New England Nuclear Corp.) source at ambient temperatures. [b] ± 0.06 mm/s. [c] ± 0.12 mm/s. [d] Frozen solution, 33% w/v in n-butylbenzene. [e] From ref. 16

to 1.1, while the value for N-trimethyltin aziridine is over 2.0 mm/s. Substitution of a 2-methyl group or increasing the ring size to four reduces the Q.S. value to an intermediate value. 2,2-Dimethyl-substitution on the aziridine ring further reduces the Q.S. value to within the 0.8–1.1 mm/s range.
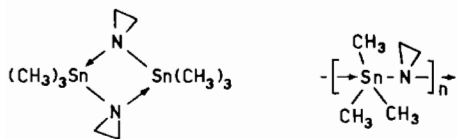
Crystalline N-trimethyltin aziridine is only moderately sensitive to hydrolysis by moist air, while its liquid dimethylamino analogue fumes. The infrared spectra of the tin aziridines are dominated by the intense, characteristic,[18] symmetric ring breathing mode at *ca.* 1240 cm^{-1}, and both the $\nu_{asym}(Sn-C)$ and $\nu_{sym}(Sn-C)$, tin–carbon stretching modes are observed in an intensity ratio no different from that of the other compounds listed in Table I. Moreover, the spectra recorded in solution do not differ from those recorded in Nujol mulls or KBr pellets, nor is the spectrum of the N-trimethyltin aziridine melt changed. In the nmr the methylene bridge protons give rise to a singe, sharp resonance

at ambient temperature indicating rapid inversion about pyramidal nitrogen in solution. Colligative measurements have indicated the monomeric nature of the stannylamines in solution,[17] but our aziridine is dimeric in benzene (osmometry: Calcd. for $C_5H_{13}NSn$, 204.7; Found, 412, 420), and the Mössbauer spectrum of a quick-frozen solution in butylbenzene at 77K is the same as that listed in Table I for the solid within experimental error.

In addition, twelve ditin fragments are found above the parent molecular ion in the mass spectrum of N-trimethyltin aziridine. The presumably cyclic ditin fragments such as $[(CH_3)_2SnNH]_2^+$ (m/e = 329; intensity = 100%), $[CH_3SnNH]_2^+$ (298; 45%) and $[SnNH]_2^+$ (268; 15%), as well as the nitrogen bridged $[Sn_2NH]^+$ (254; 13%) and monotin $[Sn(NH_2)_2]^+$ (150; 8%) are apparently portions of the associated structure of N-trimethyltin aziridine that survive transfer to the gas phase. However, ditin fragments m/e = 329 and 298 appear in the spectra of all the cyclic tin derivatives studied along with others whose number and intensity decrease with ring size. The m/e = 329 peak is the most intense feature of the mass spectra of the three tin aziridines and azetidine, each of which shows the four ditin fragments mentioned above. The observation of three ditin fragments of mass greater than that of the dimer suggests that the solid state is associated into higher oligomeric units or is a polymer.

The higher melting point and Mössbauer Q.S. value presumably also reflect the association. We predicted a nitrogen-bridged structure for trimethyltin glycinate,

$$\overset{O}{\overset{\|}{(CH_3)_3SnOCCCH_2NH_2,}}$$

on the basis of Mössbauer and infrared evidence,[19] which we have recently confirmed in an X-ray crystal structure,[20] but the association in that case gave a one-dimensional polymer with planar trimethyltin groups, while the aziridine derivative is a dimer in solution (A) and oligomeric or polymeric (B) in the solid with non-planar trimethyltin groups:

The association is broken up, however, when N-trimethyltin aziridine removes BF_3 from its etherate to form a 1:1 adduct. The insoluble, solid adduct is stable in refluxing triethylamine, but undergoes hydrolysis to liberate aziridine, which is found as the BF_3 adduct, and gives trimethyltin hydroxide.

Tin(II) diaziridine exhibits a Mössbauer resonance at ambient temperature, indicative of its associated nature.[22]

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