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N-DI- AND TRI-ORGANOTIN(IV) DERIVATIVES OF SACCHARIN

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Summary

Eleven *N*-di- and tri-organotin(IV) derivatives of saccharin, $R_nSn[NC(O)C_6H_4SO_2]_{4-n}$, where $n = 2$, R = CH_3, C_2H_5, n-C_4H_9, C_6H_5, n-C_8H_{17} and where $n = 3$, R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, C_6H_5, c-C_6H_{11} are synthesized in high yield by reaction of the corresponding organotin(IV) chlorides with the ammonium salt of saccharin in methanol. The products are colorless crystals, soluble in organic solvents. Vibrational spectroscopic band assignments are made for the ν(CO) (1710–1590 cm^{-1}), $\nu(SO_2)$ (1375–1115 cm^{-1}), ν(Sn–C) (600–500 cm^{-1}) and ν(Sn–NCO) (380–349 cm^{-1}). No fragments of mass greater than the parent molecular ion or containing more than one tin atom are seen in the mass spectra at 12 eV of any of the compounds studied. Only in the triphenyltin(IV) derivative is the parent molecular ion seen. The tin-119m Mössbauer isomer shift (*IS*) values confirm tin as tin(IV), and the quadrupole splitting (*QS*) and $\rho(QS/IS)$, values are typical of higher than four-coordination with the NMR $|^2J(^{119}Sn\text{–}C\text{–}^1H)|$ coupling constants of the methyltins in solution corroboratory. From the *QS* values of the *N*-diorganotin(IV) derivatives a point charge model is used to calculate the carbon–tin–carbon angles. The magnitudes of these angles suggest that these derivatives have a generally *trans*-R_2Sn configuration with predicted angles in the range 139–180°. The *N*-triorganotin(IV) derivatives have equatorial R_3Sn groups which are approximately planar.

Introduction

Introduction of sucrose residues into organotin pesticides is said to increase substantially the biocidal activity per unit weight of tin, and the compounds are effective against organisms not attacked by conventional organotin pesticides such as tri-n-butyltin(IV) oxide [1,2]. Other reports describe organotin(IV) derivatives of sugars [3–6]. Following obvious analogy, we have prepared a series of organotin saccharin (2,3-dihydro-3-oxobenzoisosulfonazole or 1,2-dihydro-2-ketobenzoisosulfonazole or *ortho*-sulfobenzamide or 1,2-benzoisothiazol-3(2*H*)-one) derivatives.

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(1)

One member of the series, the triethyltin derivative, has been reported from the action of triethyltin hydroxide with saccharin in ethanol [7] and characterized by m.p. (112.5–113°C) and microanalytical data.

We report in this paper the synthesis of eleven *N*-di- and tri-organotin(IV) derivatives of saccharin, and their characterization by physical properties, analysis, and infrared, Raman, mass, NMR and tin-119m Mössbauer spectroscopic data.

Experimental section

Organotin starting materials were of commercial grade and were used without further purification. Ammonium saccharin was prepared by reacting *o*-carbomethoxybenzene sulfonyl chloride with ammonium hydroxide, or by reacting the benzoyl chloride with ammonia [8].

Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Infrared spectra were recorded on a Beckman 4250 spectrometer as Nujol mulls on CsI plates. Mass spectra were recorded on a Hewlett-Packard 5985B mass spectrometer at an exciting voltage of 12 eV. Tin-119m Mössbauer spectra were recorded on a Ranger Engineering spectrometer equipped with NaI scintillation counter and using $Ca^{119m}SnO_3$ as standard reference material for zero velocity. Velocity calibration was based upon β-tin and natural iron foils. Standard, nonlinear, least-squares techniques were used to fit the data to Lorentzian curves. Raman data were recorded on a Spex Ramalog 5 instrument using an argon source at 4880 Å, and NMR data on an IBM NR-80 instrument using tetramethylsilane as the internal standard.

The compounds studied are listed with their yields, melting points, and microanalytical data in Table 1. Tin-119m Mössbauer data are listed in Table 2, mass spectral data in Tables 3 and 4, infrared and Raman data in Tables 5 and 6 and NMR data in Table 8.

Ammonium saccharin, $C_6H_4C(O)SO_2NNH_4$

O-Carbomethoxybenzene sulfonyl chloride (23.5 g, 10.0 mmol) was dissolved in distilled methanol) (150 ml). After the reaction was completed, ammonium hydroxide (13.5 ml, 10.0 mmol) was added, and the mixture refluxed for 3 h at 40°C, hypochloric acid and water were removed by continuous gentle heating and then in vacuo. The title compound was separated as colorless crystals (15.0 g, 75.0%), m.p. 77–80°C.

The procedures by which the *N*-di- and tri-organotin(IV) saccharin derivatives are prepared are illustrated for the specific examples of the di- and tri-methyl compounds below.

TABLE 1

PHYSICAL DATA FOR THE $R_nSn[\overline{NC(O)SO_2C}_6H_4]_{4-n}$ ($n = 2, 3$) DERIVATIVES

Compound	M.p. (°C)	Analyses (Found (calcd.) (%))			Yield (%)
		C	H	Sn	
$(CH_3)_3SnNC(O)SO_2C_6H_4$	100–103	33.06	3.11	32.19	57
		(34.71)	(3.76)	(34.33)	
$(C_2H_5)_3SnNC(O)SO_2C_6H_4$ [a]	110–112	39.80	4.97	32.02	40
		(41.74)	(5.08)	(31.76)	
$(n\text{-}C_3H_7)_3SnNC(O)SO_2C_6H_4$	103–107	43.07	5.60	28.05	58
		(44.68)	(5.82)	(27.62)	
$(n\text{-}C_4H_9)_3SnNC(O)SO_2C_6H_4$	102–106	46.88	5.96	25.44	64
		(48.33)	(6.57)	(25.16)	
$(C_6H_5)_3SnNC(O)SO_2C_6H_4$	100–105	55.32	3.22	22.85	85
		(56.42)	(3.57)	(22.32)	
$(c\text{-}C_6H_{11})_3SnNC(O)SO_2C_6H_4$	120–124	53.03	5.88	20.80	82
		(54.57)	(6.73)	(21.59)	
$(CH_3)_2Sn[NC(O)SO_2C_6H_4]_2$	153–156	35.98	2.60	24.01	39
		(37.44)	(2.73)	(23.15)	
$(C_2H_5)_2Sn[NC(O)SO_2C_6H_4]_2$	135–142	37.78	3.02	22.05	46
		(39.94)	(3.32)	(21.92)	
$(n\text{-}C_4H_9)_2Sn[NC(O)SO_2C_6H_4]_2$	143–146	43.28	4.11	19.92	81
		(44.24)	(4.36)	(19.88)	
$(C_6H_5)_2Sn[NC(O)SO_2C_6H_4]_2$	159–163	48.86	2.98	26.61	73
		(50.14)	(3.08)	(26.10)	
$(n\text{-}C_8H_{17})_2Sn[NC(O)SO_2C_6H_4]_2$	85–90	49.60	5.28	17.03	85
		(50.79)	(5.93)	(16.75)	

[a] Ref. 7.

Bis(2,3-dihydro-3-oxobenzoisosulfonazolo)N-dimethyltin(IV), $(CH_3)_2Sn[NCOSO_2C_6H_4]_2$

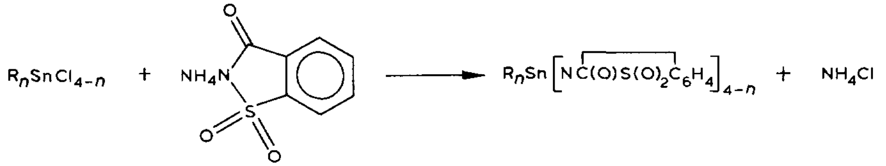
To a methanol solution (150 ml) of dimethyltin(IV) dichloride (2.20 g, 10.0 mmol), ammonium saccharin (4.00 g, 10.0 mmol) was added and the mixture refluxed for 1 h. Filtration gave a clear solution. The solvent was removed in vacuo, and ammonium chloride was removed by washing several times with distilled water to give the product as a white powder which was recrystallized twice from methanol (2.00 g, 39.1%).

2,3-Dihydro-3-oxobenzoisosulfonazolo-N-trimethyltin(IV), $(CH_3)_3SnNC(O)SO_2C_6H_4$

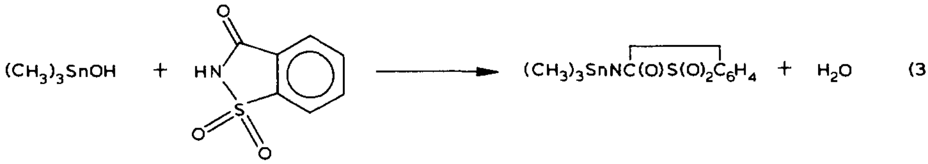
To a methanol solution (150 ml) or trimethyltin(IV) chloride (1.99 g, 10.0 mmol), ammonium saccharin (2.00 g, 10.0 mmol) was added and the mixture refluxed for 1 h. Filtration gave a clear solution and the solvent removed in vacuo. Ammonium chloride was removed by washing several times with distilled water to give the product as colorless crystals which were recrystallized twice from methanol (2.00 g, 57.1%).

Results and discussion

The syntheses of the organotin(IV) saccharin derivatives proceeds in high yield from the action of the corresponding organotin(IV) chloride and the ammonium salt of saccharin (Daramin) in refluxing anhydrous methanol:


(2)

The solvent was evaporated, the ammonium chloride removed by washing the solid residues with water and the products recrystallized from methanol. The trimethyltin derivative was also synthesized via an alternative route from the hydroxide in ethanol:


(3)

with the water produced being removed by a Dean-Stark trap. Heating the recrystallized saccharides in vacuum to just under their melting points in an Abderhalden drying pistol fails to release water. Thus the products are not merely complexes of $R_nSn(OH)_{4-n}$ with saccharine. These formulations would differ from our Sn–N bonded products by one mole of presumably releasable water.

The first question concerns whether the Sn–N bond formed in these saccharin derivatives will be robust enough to withstand hydrolysis by the water used to separate the ammonium chloride from the product. Most *N*-organotin amines are fiercely moisture-sensitive [9,10]; however, *N*-triorganostannyl derivatives in which nitrogen atoms are in 1,3-positions in a conjugated ring as in the imidazole, 1,2,3- and 1,2,4-triazole, benzimidazole and 1,2,3-benztriazole systems [11–14] are exceptions in which intermolecular association in the solid state can arise through coordination by the second nitrogen atom in the heterocycle to give a one-dimensional polymer with planar triorganotin(IV) units axially bridged by the 1,3-dinitrogen heterocycles. The associated nature of these solids is reflected in their high Mössbauer quadrupole splitting (*QS*) values (2.5–3.0 mm s^{-1}) [15,16] vs. only ca. 1.0 mm s^{-1} for the related open-chain diethylamino derivatives [17] and also in their chemical stability. Their viscous solutions in organic solvents contain oligomeric species [14,18], unlike the normally monomeric organotin(IV) amines [9,10,19]. Intermolecular association can also result when the amine moiety is of no steric bulk. Solid *N*-trimethyltin aziridine [20] (*QS* 2.44 mm s^{-1} [21], for example, is only moderately sensitive to hydrolysis in moist air, while its liquid dimethylamino analogue fumes in the atmosphere [9,10] (*QS* for $n\text{-}Bu_3SnNMe_2$ 1.08 mm s^{-1} [17]). Variable temperature Mössbauer data confirm the association [21].

A closer analogy to saccharin is found in *N*-trimethyltin(IV) succinimide whose structure we have recently solved [22]. This moisture-stable solid contains helical chains held together by coordination of one carbonyl group per heterocycle to an adjacent trimethyltin(IV) moiety. The same grouping is available in saccharin, but in these derivatives there will be competition from the SO_2 for a coordination site at tin.

Table 2 lists the tin-119m Mössbauer data for the products. The spectra are all well-resolved doublets where isomer shift (*IS*) values confirm tin as tin(IV), and the high *QS* and $\rho(QS/IS)$ values specify higher than four-coordination at the tin atom [23]. This fact demands a bridged structure utilizing nitrogen (unlikely, vide supra) or the oxygen atoms of the carbonyl or sulfoxide groups. The observation of resolvable Mössbauer spectra at ambient temperatures for two of the saccharin derivatives (triphenyl and di-n-butyltin (see Table 2)) suggests polymeric vs. oligomeric formulations in these solids.

However, the absence of peaks of greater mass than the parent molecular ions or containing more than one tin or multiples of other atoms in the mass spectra (see Tables 3 and 4) cannot be used to decide between oligomeric and polymeric structures for these materials or to distinguish carbonyl and sulfoxide association. The mass spectral fragmentation patterns are conventional, exhibiting a parent molecular ion only for the triphenyltin derivative. There is neither the preponderance of sulfur-tin or tin-oxygen combinations which would suggest which mode of coordination is being used.

While the derivatives may be monomeric in the gas phase, the coupling constants, $|^2J(^{119}\text{Sn–C–}^1\text{H})|$, in the proton NMR of the *N*-di- and tri-methyltin(IV) derivatives specify higher than four-coordination [24] in the deutero-methanol and chloroform solutions employed (see Table 8).

The observations of both ν_{asym} and ν_{sym}(Sn–C) modes in both the infrared and Raman spectra rule out precisely linear and planar di- and tri-organotin(IV) moieties, respectively. Hence, the association, whichever its nature, most not be extremely strong.

For the *N*-diorganotin(IV) saccharin derivatives a treatment based upon a point-charge model [25] links the magnitude of the *QS* values to the carbon–tin–carbon bond angle. The results correlate well with known structural data [26] for dimethyl- and diphenyl-tin(IV) systems [25,27]. The calculations, which are based upon the

(Continued on p. 232)

TABLE 2

TIN-119m MÖSSBAUER DATA FOR THE ORGANOTIN(IV) SACCHARIN DERIVATIVES AT 77 K IN mm s^{-1}

Compound	*IS* ±0.03	*QS* ±0.06	Γ_1 ±0.02	Γ_2 ±0.02	$\rho = QS/IS$	Calcd. < C–Sn–C (°) [b]
$(CH_3)_3SnNC(O)SO_2C_6H_4$	1.28	3.48	1.38	1.48	2.72	
$(C_2H_5)_3SnNC(O)SO_2C_6H_4$	1.34	3.85	1.43	1.44	2.87	
$(n\text{-}C_3H_7)_3SnNC(O)SO_2C_6H_4$	1.63	4.24	1.18	1.19	2.60	
$(n\text{-}C_4H_9)_3SnNC(O)SO_2C_6H_4$	1.05	4.10	1.22	1.21	3.90	
$(C_6H_5)_3SnNC(O)SO_2C_6H_4$	1.40	2.80	1.41	1.33	2.00	
	1.42 [a]	2.81 [a]	1.43 [a]	1.35 [a]	1.98 [a]	
$(c\text{-}C_6H_{11})_3SnNC(O)SO_2C_6H_4$	1.70	3.71	1.46	1.54	2.18	
$(CH_3)_2Sn[NC(O)SO_2C_6H_4]_2$	1.60	3.61	1.38	1.48	2.26	146
$(C_2H_5)_2Sn[NC(O)SO_2C_6H_4]_2$	1.34	3.85	1.43	1.44	2.87	156
$(n\text{-}C_4H_9)_2Sn[NC(O)SO_2C_6H_4]_2$	1.52	4.83	1.82	1.82	3.18	180
	1.58 [a]	4.86 [a]	1.83 [a]	1.81 [a]	3.11 [a]	180
$(C_6H_5)_2Sn[NC(O)SO_2C_6H_4]_2$	1.43	3.12	1.71	1.31	2.18	139
$(n\text{-}C_8H_{17})_2Sn[NC(O)SO_2C_6H_4]_2$	1.05	3.44	1.47	1.31	3.28	141

[a] Ambient-temperature data. [b] Using the point charge model (see text).

TABLE 3

MASS SPECTRAL DATA FOR THE $R_3Sn\overline{NC(O)SO_2C}_6H_4$ DERIVATIVES[a]

m/e	$(CH_3)_3SnNC(O)SO_2C_6H_4$	$(C_2H_5)_3SnNC(O)SO_2C_6H_4$	$(n\text{-}C_4H_9)_3SnNC(O)SO_2C_6H_4$	$(C_6H_5)_3SnNC(O)SO_2C_6H_4$	$(c\text{-}C_6H_{11})_3SnNC(O)SO_2C_6H_4$
533				$[(C_6H_5)_3SnNC(O)SO_2\text{-}C_6H_4]^+$ (3.3)	
468					$[C(O)SO_2NSn(C_6H_{11})_2C_6H_4]^+$ (100.0)
332	$[C_6H_4SO_2C(O)NSn\text{-}(CH_3)_2]^+$ (100.0)				$[C(O)[H_4NSn(C_6H_{11})_2]^+$ (51.5)
302	$[C_6H_4SO_2C(O)NSn]^+$				$[H_2NSn(C_6H_{11})_2]^+$(57.5)
269			$[SOC(O)NSn(C_4H_9)H_2]^{+\cdot}$ (10.0)		
253	$[C(O)SO_2NSnC_2H_3]^{+\cdot}$		$[SC(O)Sn(C_4H_9)H_2]^+$ (100.0)		
212	$[CH_3SnNSO_2\text{-}H]^+$ (10.7)				
213		$[C_2H_5SnNSOH_2]^{+\cdot}$(100.0)			
183	$[SnNSOH]^{+\cdot}$ (86.1)			$[HSONSn]^+$ (86.1)	
177			$[SnC_4H_9]^+$ (18.9)		
165	$[Sn(CH_3)_3]^{+\cdot}$ (40.7)				
154				$[SSnH_2]^+$ (100.0)	
135	$[SnCH_3]^{+\cdot}$ (46.3)				
120	$[SnCH_3]^{+\cdot}$ (57.5)	$Sn^{+\cdot}$ (57.6)	$Sn^{+\cdot}$ (0.9)	$Sn^{+\cdot}$ (38.1)	$Sn^{+\cdot}$ (0.5)

[a] Only tin-bearing fragments are listed. Mass numbers are based upon ^1H, ^{12}C, ^{14}N, ^{16}O, ^{32}S and ^{120}Sn.

TABLE 4

MASS SPECTRAL DATA FOR THE $R_2Sn[\overline{NC(O)SO_2C}_6H_4]_2$ DERIVATIVES[a]

m/e	$(CH_3)_2Sn[NC(O)SO_2C_6H_4]_2$	$(C_2H_5)_2Sn[NC(O)SO_2C_6H_4]_2$	$(n\text{-}C_4H_9)_2Sn[NC(O)SO_2C_6H_4]_2$	$(C_6H_5)_2Sn[NC(O)SO_2C_6H_4]_2$	$(n\text{-}C_8H_{17})_2Sn[NC(O)SO_2C_6H_4]_2$
360		$[(C_2H_5)_2Sn(NCOSO_2)_2H]^+$ (9.4)			
332	$[C_6H_4SO_2C(O)NSn(CH_3)_2]^+$ (100.0)				
302	$[C_6H_4SO_2C(O)NSn]^+$ (44.9)	$[Sn(NCOSO_2)_2H]^+$ (100.0)			
249			$[(C_4H_9)_2SnNH]^{+\cdot}$ (20.4)		
238		$[Sn(NCO)_2SO_2H]^+$ (17.7)			
234			$[(C_4H_9)_2SnH_3]^{+\cdot}$ (17.7)		
212	$[SnN_2SO]^+$ (16.9)		$[SnN_2SO_2]^+$ (100.0)		
210		$[(C_2H_5)_2SnN_2H_2]^+$ (18.3)			
197	$[SnNSO_2-H]^{+\cdot}$ (12.8)				
196			$[SnNSO_2-H]^{+\cdot}$ (90.9)		
183	$[SnNSOH]^{+\cdot}$ (50.6)	$[SnNSOH]^+$ (26.9)	$[SnNSOH]^{+\cdot}$ (28.9)	$[SnNSOH]^{+\cdot}$ (45.9)	$[SnNSOH]^{+\cdot}$ (100.0)
167			$[SnNSH]^+$ (20.8)		
165					
162	$[SnNC(O)]^+$ (39.4)	$[SnNCO]^+$ (24.4)			
154				$[SSnH_2]^-$ (100.0)	
135	$[SnCH_3]^{+\cdot}$ (39.0)		$[SnNH]^{+\cdot}$ (8.9)		
120	$Sn^{+\cdot}$ (33.8)	$Sn^{+\cdot}$ (21.0)	$Sn^{+\cdot}$ (5.5)	$Sn^{+\cdot}$ (15.0)	$Sn^{+\cdot}$ (18.9)

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[a] Only tin-bearing fragments are listed. Mass numbers are based upon ^1H, ^{12}C, ^{14}N, ^{16}O, ^{32}S and ^{120}Sn.

assumption that the contribution of the ligands to the electric field gradient at the tin atom is negligible, yields the angles listed in Table 2. The angle of 146° for the dimethyltin(IV) saccharin is consistent with the observation of a ν_{sym}(Sn–C) mode in the infrared and a ν_{asym}(Sn–C) mode in the Raman spectra. From the magnitudes of the angles, the *N*-diorganotin(IV) derivatives are in a roughly *trans*-R_2Sn configuration.

Triorganotin compounds with a trigonal bipyramidal geometry have small *QS* values if one of the three organic groups is at an apical position [28]. The *QS* values for the aliphatic triorganotin(IV) saccharin derivatives are 3.48–4.24 mm s^{-1} and 2.80 mm s^{-1} for the triphenyltin(IV) derivative, and so we conclude that the C_3Sn unit is equatorial and rather flat in these derivatives.

Intramolecular coordination of the tin atoms by oxygen from the carbonyl or sulfoxide groups requires making four-membered rings and can be ruled out. Coordination by the nitrogen atom apparently only occurs in organotin(IV)-nitrogen derivatives when the steric requirements at the nitrogen are negligible, as in *N*-trimethyltin(IV) azide which bridges through the α-nitrogen atom of the azide group [29,30], or in *N*-trimethyltin(IV) aziridine [21], and so can also be ruled out. In any case, coordination to a metal by amide systems is always through the oxygen of the carbonyl group [31], and coordination through an oxygen atom of the N-SO_2-system would likewise be expected.

The decision whether the $>$C=O or $>SO_2$ oxygen atoms coordinate to tin in the absence of structural data can in principle be based upon evidence from vibrational spectra. Coordination to the tin atom is expected to reduce the ν(C=O) and ν(S=O) frequencies. Complexes of amides and sulfoxides with organotin(IV) halides are known [32], and available structural data [26] for DMF [33,34] and DMSO [34–37] complexes confirm that the coordination to the tin atom is by the oxygen. Hence, each of the two potential forms of binding is possible.

TABLE 5

INFRARED SPECTRAL FREQUENCIES OF THE $C_6H_4NC(O)SO_2NH_4$ AND $R_2Sn[NC(O)SO_2C_6H_4]_2$ DERIVATIVES

Compound	Infrared absorptions (cm^{-1}) [a]
$C_6H_4C(O)SO_2N^-\ NH_4^+$	1608w, 1555w, 1440s, 1365m, 1290vw, 1240vw, 1136vw, 940m, 740m, 700sh, 668vw, 580vw, 515vw, 374s, 349w, 334w, 275s.
$(CH_3)_2Sn[NC(O)SO_2C_6H_4]_2$	1854vw, 1708s, 1616s, 1572m, 1440vw, 1364s, 1328s, 1286m, 1250m, 1170s, 1136sh, 1114m, 1045w, 1009vw, 950w, 886w, 78-s, 750s, 710s, 580s, 540s, 500s, 373s, 358s, 346m, 290s, 264vw, 246vw.
$(C_2H_5)_2Sn[NC(O)SO_2C_6H_4]_2$	1710m, 1625w, 1446s, 1368s, 1330m, 1292sh, 1250w, 1174m, 1138sh, 1115vw, 1010vw, 950m, 890vw, 716sh, 678m, 580m, 520m, 369sh, 359w, 343m, 298s, 265m, 235vw.
$(n\text{-}C_4H_9)_2Sn(NC(O)C_6H_4]_2$	1575sh, 1375s, 1295vw, 1255vw, 1150m, 1126sh, 1080vw, 958vw, 874vw, 680vw, 556sh, 364w, 346w, 308w, 244vw.
$(C_6H_5)_2Sn[NC(O)SO_2C_6H_4]_2$	1625m, 1592m, 1370s, 1288w, 1245w, 1155m, 1130s, 10102, 946w, 798vw, 675w, 546m, 375m, 337w, 302w, 270w.
$(n\text{-}C_8H_{17})_2Sn[NC(O)SO_2C_6H_4]_2$	1710s, 1628sh, 1580vw, 1370s, 1330s, 1284m, 1249m, 1170s, 1134sh, 1120m, 890w, 750m, 714m, 670m, 570s, 508s, 372vw, 358m, 346m, 332w, 288s, 264w, 222sh.

[a] s = strong, b = broad, v = very, w = weak, m = medium, sh = shoulder.

TABLE 6

INFRARED SPECTRAL FREQUENCIES OF THE $\mathrm{R_3Sn\overline{NC(O)SO_2C}_6H_4}$ DERIVATIVES

Compound	Infrared absorptions ($\mathrm{cm^{-1}}$) [a]
$\mathrm{(CH_3)_3SnNC(O)SO_2C_6H_4}$	1660vs, 1590vs, 1340sh, 1320sh, 1290vs, 1200m, 1160vs, 1115vs, 960vs, 750vs, 770vs, 590vs, 520vs, 380vs, 354w, 340s, 320m, 299s, 260m.
$\mathrm{(C_2H_5)_3SnNC(O)SO_2C_6H_4}$	1608w, 1556w, 1366vs, 1290m, 1253m, 1183sh, 1140m, 1109sh, 1040w, 1008w, 946m, 749m, 666m, 590w, 500w, 373vw, 360vw, 373s, 300vw, 275vw, 250w, 224vw.
$\mathrm{(n\text{-}C_3H_7)_3SnNC(O)SO_2C_6H_4}$	1720vw, 1635m, 1576m, 1370s, 1328w, 1290m, 1250m, 1150m, 1115w, 990vw, 954m, 774vw, 750w, 715vw, 670m, 582m, 515vw, 375vw, 360m, 338m, 299m, 276m, 260vw, 225vw.
$\mathrm{(n\text{-}C_4H_9)_3SnNC(O)SO_2C_6H_4}$	1621m, 1575w, 1370s, 1333sh, 1283w, 1250w, 1146m, 1116sh, 1070m, 1010vw, 955m, 865m, 750sh, 690sh, 668m, 599w, 500vw, 349m, 335s, 304s, 266vw, 230vw.
$\mathrm{(c\text{-}C_6H_{11})_3SnNC(O)SO_2C_6H_4}$	2650vw, 1670m, 1625m, 1440vw, 1370s, 1328sh, 1300m, 1265w, 1225w, 1162s, 1145sh, 1116w, 1070vw, 984m, 950m, 870vw, 832vw, 775w, 740m, 668vw, 575vw, 370w, 358w, 364vw, 332vw, 318vw, 290w, 265vw, 235vw.
$\mathrm{(C_6H_5)_3SnNC(O)SO_2C_6H_4}$	1620vw, 1570vw, 1425vw, 1370vw, 1299vw, 1248vw, 1148vw, 1110vw, 1070w, 990vw, 950vw, 690m, 600vw, 368vs, 350s, 334vw, 300vw, 274s, 256vw, 220vw.

[a] s = strong, b = broad, v = very, w = weak, m = medium, sh = shoulder.

TABLE 7

SOME IR AND RAMAN [a] SPECTRAL ASSIGNMENTS FOR THE $\mathrm{R_nSn[\overline{NC(O)SO_2C}_6H_4]_{4-n}}$ (n = 2, 3) DERIVATIVES

Compound	ν(CO)	ν(Sn–NCO)	$\nu(\mathrm{SO_2})$	ν(Sn–C)
$\mathrm{(CH_3)_3SnNCOSO_2C_6H_4}$	1660vs	380vs	1340sh	590vs (592vw)
	1590vs	354w	1160vs	520vs (519w)
$\mathrm{(C_2H_5)_3SnNCOSO_2C_6H_4}$	1638w	373vw	1366vs	590w
		360vw	1140m	500
$\mathrm{(n\text{-}C_3H_7)_3SnNCOSO_2C_6H_4}$	1720vs	375vw	1370s	582m
	1635m		1150m	515vw
$\mathrm{(n\text{-}C_4H_9)_3SnNCOSO_2C_6H_4}$	1621m	349m	1370s	590w
			1146m	500vw
$\mathrm{(c\text{-}C_6H_{11})_3SnNCOSO_2C_6H_4}$	1625m	370w	1370s	570vw
		358w	1162s	
$\mathrm{(C_6H_5)_3SnNCOSO_2C_6H_4}$	1620vw	378vs	1370vw	600vw
			1148vw	
$\mathrm{(CH_3)_2Sn[NCOSO_2C_6H_4]_2}$	1708s	373s	1364s	580s (575m)
	1616s	358s	1170s	540s (519w)
$\mathrm{(C_2H_5)_2Sn[NCOSO_2C_6H_4]_2}$	1710m	369sh	1368s	580m
	1625w	359w	1174m	520m
$\mathrm{(n\text{-}C_4H_9)_2Sn[NCOSO_2C_6H_4]_2}$	1630m	364w	1375s	556sh
			1150m	
$\mathrm{(C_6H_5)_2Sn[NCOSO_2C_6H_4]_2}$	1625m	375m	1370s	546m
			1155m	
$\mathrm{(n\text{-}C_8H_{17})_2Sn[NCOSO_2C_6H_4]_2}$	1710s	372vw	1370s	570s
	1628sh		1170s	508s

[a] Raman data are in parentheses.

TABLE 8

^1H NMR DATA FOR $(CH_3)_2Sn[\overline{NCOSO_2C}_6H_4]_2$ AND $(CH_3)_3Sn\overline{NC(O)SO_2C}_6H_4$ RELATIVE TO TMS

	$\vert ^2J(^{119}Sn\text{-}C\text{-}^1H)\vert$ (Hz)	δ (^1H) (ppm)
$(CH_3)_2Sn[NC(O)SO_2C_6H_4]_2$	80.0 [a]	0.44 [a]
	79.0 [b]	0.40 [b]
$(CH_3)_3SnNC(O)SO_2C_6H_4$	79.0 [a]	0.39 [a]
	77.0 [b]	0.36 [b]

[a] In deuteromethanol. [b] In deuterochloroform.

Tables 5 and 6 list the infrared absorptions for the di- and tri-organotin(IV) saccharin derivatives, ant Table 7 lists the assignments of these and the Raman absorptions to the ν(CO), $\nu(SO_2)$, ν(Sn–C) and ν(Sn–NCO) modes, in order of decreasing frequency. The ν_{asym} and $\nu_{sym}(SO_2)$ modes have been assigned in solid saccharin itself at 1377 and 1164 cm^{-1}, respectively [38]. Attachment of the heavy organotin group to the adjacent nitrogen atom would be expected by itself, however, to move these and the carbonyl absorptions to lower frequency. In any case there appears to be no discernable trend of changes in the absorptions assigned to the $\nu(SO_2)$ and ν(CO) modes to lower frequency from the data in Table 7. Hence, the use of these values to decide whether it is the carbonyl or the sulfonyl oxygen atoms (or both) which are coordinated to the tin in our derivatives is ruled out.

Better guidance on this point comes from the results of structural studies on other metal saccharides. The systems for which data are available refer for the most part to metal cation complexes, but a mercury(II) derivative may be covalently bonded. The known structures include: $C_7H_4NO_3SNa \cdot 2/3H_2O$ [39], $(C_7H_4NO_3S)_2Mg \cdot 7H_2O$ [39], $(C_7H_4NO_3S)Mn \cdot 6H_2O$ (isomorphous with the Fe, Co, Ni, Zn and Cd complexes) [40], $(C_7H_4NO_3S)_2Hg$ [41] and $(C_7H_4NO_3S)_2Cu(H_2O)_4 \cdot 2H_2O$ [42]. These data establish: (i) the presence of the metal–nitrogen bond, even in the presence of water (Na^+, Mn^{2+}, Hg^{2+} and Cu^{2+}); (ii) that both the carbonyl and the sulfonyl oxygen atoms are capable of binding to the metal (Na^+ and Hg^{2+}); and (iii) when only one type of oxygen atom binds, the carbonyl binds alone (Mg^{2+}), and when both types bind, the carbonyl oxygen atoms bind at shorter distances (Na^+, Hg^{2+}). Thus binding by the carbonyl oxygen atom is the preferred mode of coordination in these analogous systems, and we conclude that our tin atoms are coordinated through either (i) both C=O and S=O groups, or (ii) through the C=O groups alone in these products as well.

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