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Organotin mediated cycloaddition reactions: a re-investigation of the reaction between organotin azides and isothiocyanates

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Abstract

Organotin derivatives of 1-organo-5-thiotetrazole (RN_4CS) have been synthesised by two methods: (i) a cycloaddition reaction between Bu_3SnN_3 and RNCS, and (ii) reaction between the sodium salt of the preformed tetrazole and an organotin halide. The structure of $Bu_2Sn(SCN_4Ph)_2$ has been determined, and the ligand shown to be in the thio form, attached to tin through sulphur, rather than through nitrogen as previously reported. An analysis of the azide-isothiocyanide cycloaddition reaction based upon molecular orbital calculations is presented.

Introduction

Organotin azides are well known 1,3-dipolar reagents that have a number of uses, including the synthesis of tetrazoles [1] and triazoles [2] through [3 + 2] cycloaddition reactions, nitriles and alkynes being the dipolarophiles in the two quoted examples. We have recently shown that such cycloaddition reactions result in tin-substituted heterocycles, in which the tin confers unexpected reactivity on the ring atoms. In this way, a one-pot cycloaddition reaction between Bu_3SnN_3 and $Ph_3Sn(CH_2)_3CN$ yields initially (N-tributylstannyl)$Ph_3Sn(CH_2)_3CN_4$ (CN_4 = tetrazole), and subsequently the bicyclic product (I) via an intramolecular cyclisation process involving elimination of Bu_3SnPh [3].

In the light of this work, we became interested in cycloaddition reactions between organotin azides and organic isothiocyanates, first reported by Dunn and Oldfield some years ago [4]. Such reactions are of interest for two reasons. Firstly, the dipolarophile is the C=N functionality, yielding II, in contrast to the analogous reaction involving hydrogen azide which adds to the C=S moiety to give 5-phenylamino-1,2,3,4-thiatriazole (III) [5]. Secondly, the thiophilicity of tin is well known,

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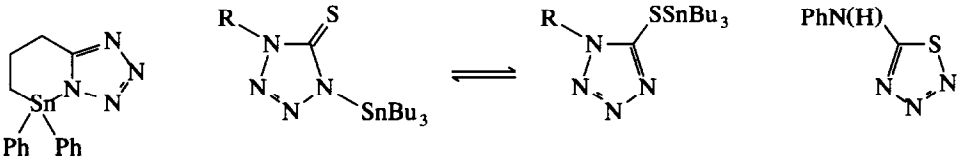
and the products initially formulated in the thione form (IIa) could equally plausibly exist in tautomeric form (IIb). In this paper we report the synthesis of several new organotin derivatives of 1-organo-5-thiotetrazole, and confirm that the products of such cycloaddition reactions do, indeed, have the thiol form (IIb).



(I) (IIa) (IIb) (III)

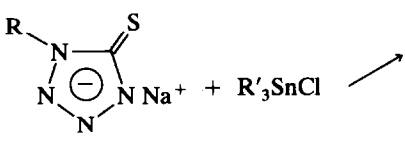
Results and discussion

Organotin derivatives of 1-organo-5-thiotetrazoles have been synthesised both by the cycloaddition between an organotin azide and an organic isothiocyanate (eq. 1), or by simple metathesis between an organotin chloride and the sodium salt of the preformed tetrazole (eqs. 2 and 3). Product **3** was made by both methods, and the products showed identical physical properties (including no depression of melting point for a mixed sample), and both had the same melting point as previously reported [4]. This rules out any structural differences in products which could accrue from having preformed the heterocycle before tin substitution, as against forming the heterocycle from a tin-containing reagent.

The cycloaddition reactions are remarkably facile, with both products **1** and **3** separating as white crystalline solids when a mixture of the two respective reagents is kept for 24 h at room temperature.

The metathesis reactions were carried out in refluxing ethanol, with the organotin product being separated from the NaCl also produced in the reaction by recrystallisation from hexane/chloroform (10:1). Somewhat surprisingly, reaction between Me_2SnCl_2 and two equivalents of the 1-phenyl-5-thiotetrazolate anion yielded only the partially substituted dimethylchlorotin product (**7**) (eq. 4).

$$RNCS + R'_3SnN_3 \rightarrow \text{(IIa)} \rightleftharpoons \text{(IIb)} \quad (1)$$



$$\xrightarrow{+\ R'_3SnCl} \quad (2)$$

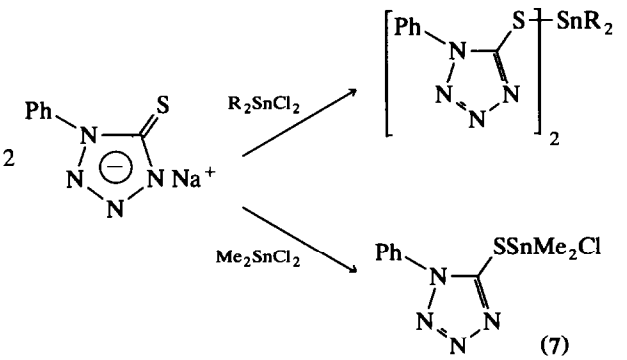
	1	2	3	4
R	Me	Ph	Ph	Ph
R'	Bu	Me	Bu	Ph

Table 1

Spectroscopic data

	$\delta(^{119}Sn)$ [a]	^1J(Sn–C) (Hz)	^2J(Sn–H) (Hz)	IS (mm s^{-1})	QS (mm s^{-1})	$\Gamma_{1,2}$ [b] (mm s^{-1})
1	112.5	328.3		1.48	3.32	0.90, 0.91
2 [c]	109.8	383.4	60.4	1.36	3.14	0.90, 0.93
3	116.6	330.5		1.48	3.30	0.88, 0.89
4	−69.4			1.33	2.38	0.88, 0.91
5	−27.7	418.4		1.50	2.99	0.88, 0.84
6	−145.3			1.47	3.76	0.94, 0.97
7 [d,e]	39.4	484.7	71.6	1.47	3.37	0.89, 0.90

[a] ppm relative to Me_4Sn. [b] Full width at half height. [c] ν(Sn–C) 540, 500 cm^{-1}. [d] ν(Sn–C) 550, 500 cm^{-1}. [e] ν(Sn–Cl) 300 cm^{-1}.



	5	6
R	Bu	Ph

(3)

(4)

Spectroscopic evidence distinguishing thione and thiol isomers (IIa,b) is limited, but the infrared spectra of all the compounds lack the ν(C=S) band at 1110 cm^{-1}, suggesting that the thiol tautomer is most likely. Crystallographic analysis of **5** confirmed this supposition (see below). Structurally, N-bonded organotin tetrazoles are polymeric materials in which tin adopts a 5-coordinated *trans*-N_2SnR_3 geometry. Support for this assertion comes from early concentration dependent viscosity measurements [1] and more recent NMR [6] and crystallographic [7] studies. In contrast, Sn–S bonded compounds are less Lewis acidic and are often four-coordinate in nature [8]. For example, (*S*-tricyclohexylstannyl)-2-mercaptobenzothiazole, which has ligand similarity to the current compounds, adopts such a coordination number [9]. Spectroscopic data for the compounds studied are given in Table 1. Compounds **1–4** are all tetrahedral monomers in solution, as specified by their downfield ^{119}Sn chemical shift values. Comparison with chloroform solutions of Me_3SnCl [$\delta(^{119}Sn)$ 164.2 ppm] or Ph_3SnCl (−44.7 ppm) serves to endorse this interpretation [10]. The angle C–Sn–C calculated from the available relationships with ^1J(Sn–C) and ^2J(Sn–C–H) (Table 2) confirms this assignment [11–13]. In the solid state, however, **1–3** all exhibit Mössbauer quadrupole splitting (QS) data consistent with a *trans*-$SNSnR_3$ arrangement (IV), which presumably arise from intermolecular interactions given the four-coordinate nature of the compounds in solution. Such interactions must be weaker than in related N-bonded tetrazoles $R_3Sn(N_4C)$ from the fact that $\nu_{symm,asymm}$(Sn–C) at 540, 500 cm^{-1}, respectively, are visible in the infrared spectrum of **2**, implying non-planarity of the C_3Sn moiety. QS data also imply that **4** retains its tetrahedral nature in the solid

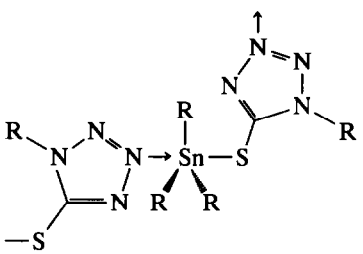
Table 2

C–Sn–C angles (°) calculated from spectroscopic data

	^{1}H [a]	^{13}C [b]	QS [c]
1		107.5	
2	112.4	110.4	
3		107.8	
5		116.6	127.5 [d]
6			171.0
7	119.3	121.4	

[a] Calculated using the equation of ref. 11. [b] Calculated using the equation of refs. 12 or 13, as appropriate. [c] Calculated using the equation of ref. 15. [d] Observed 130.7°.

state, paralleling the structure of tricyclohexylstannyl mercaptobenzothiazole mentioned earlier [9].



(IV)

Of the two diorganotin compounds, **5** exhibits a more upfield chemical shift than, for example, $Bu_2Sn(SEt)_2$ (123 ppm), suggesting some additional coordination about tin, but not nearly as marked an upfield shift as $Bu_2Sn(S_2CNR_2)_2$ (approx. −300 ppm) [14]. The angle C–Sn–C (Table 2) calculated from the ^{1}J(Sn–C) coupling (116.6°) also implies that additional coordination is weak, but is something of an underestimate when compared with the crystallographically determined value of 130.7°. A better estimate of this angle can be derived from the Mössbauer QS data using the model of Bancroft [15], which gives a value of 127.5°. This is a little unusual, as the Mössbauer approach is generally the more inaccurate of the two. Moreover, the coupling constant for bis-(2-thio-5-nitropyridine)-*S*-dibutylstannane [^{1}J(Sn–C) = 523 Hz], which has an almost identical structure to **5** (see below), yields a calculated angle (127°) in excellent agreement with that observed (129°) [16]. The ^{119}Sn chemical shift for **6** also implies essentially tetrahedral coordination about tin in solution {*cf.* $Ph_2Sn(SMe)_2$ and $Ph_2Sn(S_2CNR_2)_2$, $\delta(^{119}Sn)$ = 38.5 and −480 ppm, respectively [14]}, but the enhanced QS value clearly suggests a higher coordination number in the solid state. Using the methodology of Bancroft [15], the QS value affords a C–Sn–C angle of 171°, that is an almost perfectly regular *trans*-$R_2SnS_2N_2$ stereochemistry. Clearly these data can only be compatible if the enhanced coordination arises from intermolecular interactions.

The upfield chemical shift of **7** compared with **3**, and the C–Sn–C angle calculated from both ^{1}J and ^{2}J couplings (approx. 120°) are consistent with a cis-arrangement of methyl groups in a trigonal bipyramidal topology, and a similar

Table 3

Fractional atomic coordinates and equivalent isotropic thermal parameters ($Å^2$)

Atom	x	y	z	U_{eq}
Sn1	0.50000	0.05657(15)	0.25000	0.0601(9)
S1	0.54929(3)	0.24404(4)	0.34057(2)	0.0719(3)
N1	0.60230(7)	0.16187(12)	0.48257(6)	0.0556(8)
N2	0.61630(7)	0.04162(15)	0.52037(6)	0.0579(8)
N3	0.60043(8)	−0.05873(15)	0.47570(8)	0.0712(9)
N4	0.57441(8)	−0.00704(13)	0.40703(8)	0.0714(9)
C1	0.37553(11)	−0.03523(18)	0.25748(11)	0.0871(13)
C2	0.31550(13)	0.06395(20)	0.28804(12)	0.1046(15)
C3	0.22900(12)	−0.00652(20)	0.29986(10)	0.0919(13)
C4	0.16657(15)	0.09653(23)	0.32570(14)	0.1448(21)
C5	0.57669(9)	0.12674(15)	0.41297(8)	0.0582(10)
C6	0.61348(8)	0.29438(14)	0.51696(6)	0.0421(8)
C7	0.66348(9)	0.39891(15)	0.49739(7)	0.0550(9)
C8	0.66800(10)	0.52885(18)	0.52529(9)	0.0697(11)
C9	0.62971(11)	0.55134(20)	0.58211(9)	0.0801(12)
C10	0.57898(10)	0.44694(22)	0.60144(7)	0.0772(11)
C11	0.57170(10)	0.31517(18)	0.57020(9)	0.0751(11)

situation is implied by the Mössbauer QS value. Given that ligand chelation by N and S would involve a strained four-membered SnSCN heterocycle, the simplest structural arrangement consistent with a coordination number of five in both solid and solution states is a dimer, bridged either through chlorine or the nitrogen atoms of the tetrazole.

The structure of (*S*-dibutylstannyl)-bis-(1-phenyl-5-thiotetrazole)

The crystallographically determined structure of **5** is shown in Fig. 1. The structure confirms the thiol form of the ligand, in contast to the thione form previously reported [4]. Indeed, the reaction of compounds such as II with acids to

Table 4

Selected bond lengths (pm) and angles (°)

Sn1–S1	247.7(4)	Sn1–C1	210(2)
S1–C5	176(2)	N1–N2	135(2)
N1–C5	134(2)	N1–C6	143(2)
N2–N3	128(2)	N3–N4	137(2)
N4–C5	129(2)	C1–C2	155(2)
C2–C3	154(2)	C3–C4	155(3)
C1–Sn1–S1	109.3(5)	C1–Sn1–C1′	130.7(4)
C5–S1–Sn1	93.2(5)	S1–Sn1–S1′	86.6(2)
C5–N1–N2	107(1)	C6–N1–N2	122(1)
C6–N1–C5	131(1)	N3–N2–N1	108(1)
N4–N3–N2	110(1)	C5–N4–N3	106(1)
C2–C1–Sn1	113(1)	C3–C2–C1	114(1)
C4–C3–C2	113(2)	N1–C5–S1	125(1)
N4–C5–S1	125(1)	N4–C5–N1	109(1)

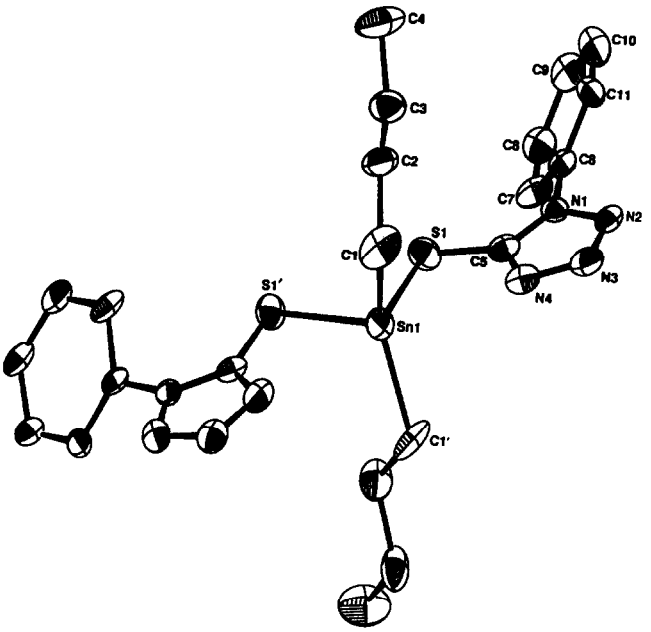


Fig. 1. The asymmetric unit of (*S*-tributylstannyl)-bis-(1-phenyl-5-thiotetrazole) (**5**) showing atomic labelling. Primed atoms are related to their unprimed counterparts (x, y, z) by $-x$, y, $0.5-z$.

give 5-thiol-substituted tetrazoles [16] can now be readily understood. The Sn–S bond (247.7 pm) is typical, and compares favourably with the analogous bond in related compounds, in particular bis-(2-thio-5-nitropyridine)-*S*-dibutylstannane (247.7 pm) with which it shows striking structural similarities [17]. The two halves of the molecule are related by a two-fold axis through the metal in the S1–Sn1–S1′ plane, and bisecting the C–Sn–C angle. The coordination about tin is essentially tetrahedral, with two weak intramolecular Sn · · · N interactions (299 pm) distorting the coordination towards *trans*-$R_2SnS_2N_2$. The opening of the C–Sn–C angle to 130.7° reflects the weakness of these interactions, though this angle is larger than in the 2-thiopyridine complex mentioned above (129.2°) despite the fact that in this latter case the Sn · · · N interactions are somewhat shorter (277 pm) [17].

The bond lengths within the tetrazole ring show the expected pattern of two short (127.5, 129.1 pm) and three long bonds (134.1, 135.4, 137.3 pm), though the errors associated with these measurements (1.5 pm) obscure any subtle bonding features.

Molecular orbital analysis of the azide-isothiocyanate cycloaddition reaction

Molecular orbital calculations were carried out on reactions involving N_3^- or Me_3SnN_3 with either PhNCS or MeNCS using the standard semi-empirical PM3 Hamiltonian as implemented in the MOPAC version 6.0 package [18]. Minimum energy geometries were determined computationally. For N_3^- and MeNCS no constraints were applied, while for PhNCS the C–C bond lengths were constrained to be the same, as were the C–H distances. A similar procedure was adopted for the C–H and Sn–C bonds in Me_3SnN_3.

Table 5

Calculated molecular orbital energies (eV)

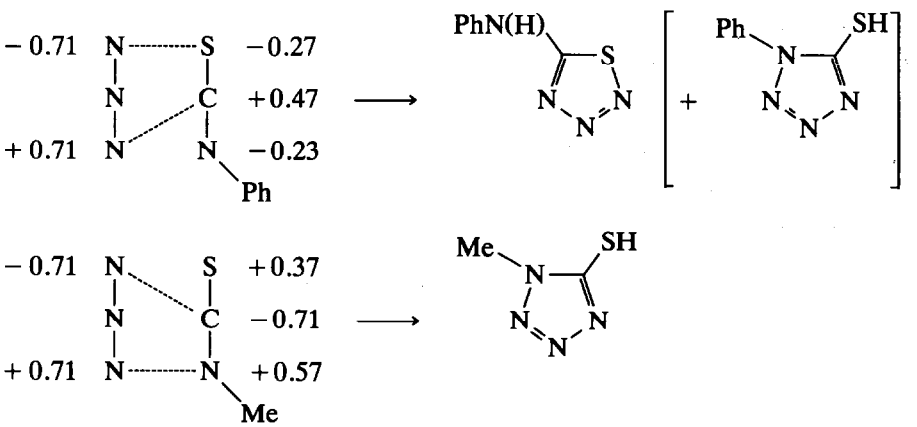
Molecule	*E*(HOMO)	*E*(LUMO)
N_3^-	−2.21216	8.80841
Me_3SnN_3	−9.81941	0.67779 (NNNLUMO)
PhNCS	−8.86751	−0.76131
MeNCS	−9.15165	0.30994 (NNLUMO)

Examination of the reactions between the above four species focuses on the frontier orbitals. For N_3^- and PhNCS, the LUMO is the opposite phase symmetry match of the HOMO, while for MeNCS the HOMO finds its partner two levels above the LUMO (the NNLUMO) and for Me_3SnN_3 three levels above the LUMO (the NNNLUMO). The relevant energies are given in Table 5.

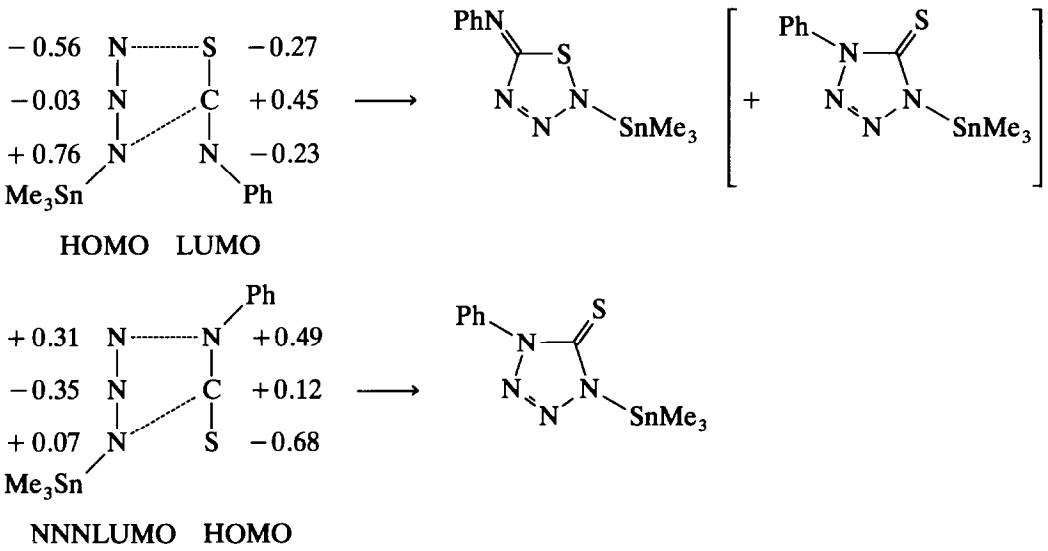
The nature of the frontier-orbital control of reaction mechanism depends, initially, on the HOMO-LUMO gap. The HOMO of N_3^- is very high due to the overall negative charge, hence reaction between N_3^- (as NaN_3) and RNCS is HOMO(N_3^-)-LUMO(RNCS). In contrast, the frontier orbital energies of Me_3SnN_3 are more closely matched to those of the isothiocyanate, and there is less than 0.5 eV difference between the HOMO(N_3^-)-LUMO(RNCS) energy gap and the corresponding LUMO(N_3^-)-HOMO(RNCS) value. Hence, both possibilities need to be considered.

Following the methodology of Fleming [19], once a choice between the two possible frontier orbital combinations is made, the predicted reaction is then based on the relevant MO coefficients which are matched biggest to biggest and smallest to smallest, while simultaneously ensuring that the relative phases on the HOMO and LUMO match.

For the N_3^--PhNCS reaction which is HOMO-LUMO controlled, the –NCS coefficients favour azide addition across the S=C dipolarophile, yielding the thiatriazole (Scheme 1), contrary to experimental observation. However, the difference between S and N orbital coefficients is very small (0.04) suggesting that the competing formation of the tetrazole should also be important. The latter, is, in



Scheme 1.



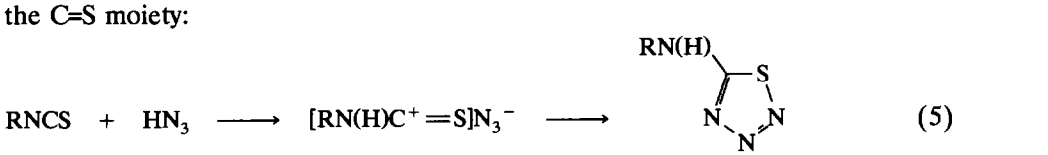
Scheme 2.

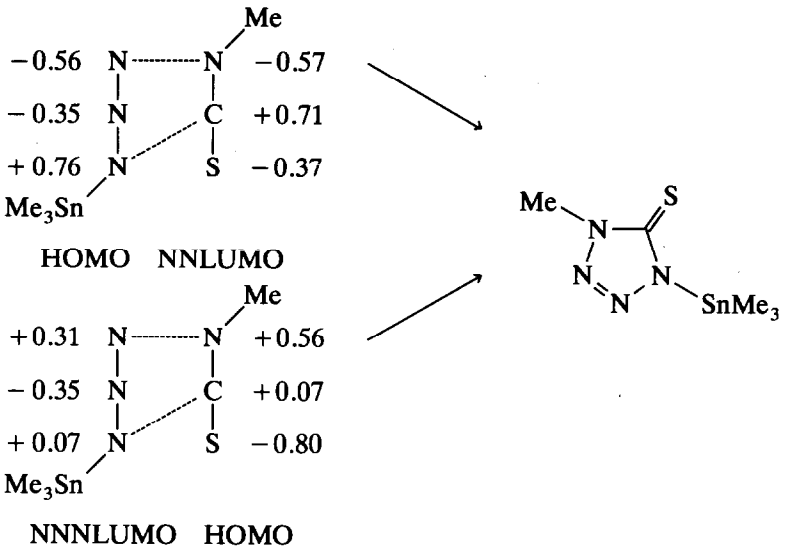
fact, the observed product [16]. The calculations apparently overestimate the sulphur contributions to the frontier functions (see also below). In contrast, the HOMO-LUMO controlled reaction of N_3^- and MeNCS correctly predicts tetrazole formation (Scheme 1), in agreement with experiment [16].

For the reactions between Me_3SnN_3 and either PhNCS or MeNCS, both HOMO-LUMO and LUMO-HOMO combinations need to be evaluated, since the two are very close in energy. For the former reaction, the same comments apply to the HOMO(Me_3SnN_3)-LUMO(PhNCS) combination as have been made to the HOMO-LUMO combination for the N_3^--PhNCS reaction. That is, thiatriazole is incorrectly predicted as the reaction product, though again the prediction is based on only a small difference in the orbital coefficients on S and N. In contrast, the LUMO(Me_3SnN_3)-HOMO(PhNCS) has only one outcome based on symmetry considerations, and that is the formation of the tetrazole, as observed experimentally (Scheme 2). Thus, on balance, the observed formation of a tetrazole is correctly predicted, though, as stated above, the role of sulphur in the LUMO of PhNCS seems to be overestimated.

The two frontier orbital combinations for the Me_3SnN_3–MeNCS reaction are shown in Scheme 3. Interestingly, in these cases both predict the same product, the observed tetrazole, irrespective of the nature of the frontier orbital control.

None of the calculations described above clearly predict the formation of the thiatriazole ring, though this is the observed product from the reaction of HN_3 and NCS [16]. Thus, as previously suggested [16], this reaction takes a different course from those described, with the initial step being protonation of the organic isothiocyanate, affording a more favourable charge neutralising cycloaddition on the C=S moiety:





Scheme 3.

Experimental

Spectra were recorded on the following instruments: Jeol GX270 (^{1}H, ^{13}C NMR), Jeol GX400 (^{119}Sn NMR). Details of our Mössbauer spectrometer and the related procedures are given elsewhere [20]. NMR spectra were recorded with saturated $CDCl_3$ solutions at room temperature.

Bu_3SnN_3 was prepared by the published method [21]. MeNCS and PhNCS were of commercial origin and were distilled before use. Organotin compounds were also purchased, except for Me_3SnCl, which was prepared from Me_4Sn and $SnCl_4$ in the usual manner [22].

Synthesis of (S-tributylstannyl)-1-phenyl-5-thiotetrazole (3): method 1

Tributyltin azide (2.0 g, 7 mmol) and phenylisothiocyanate (0.7 ml, 6 mmol) were mixed and allowed to stand at room temperature for 24 h, during which time the mixture solidified. The solid was recrystallised from hexane/chloroform (10:1) to give the product as white crystals (2.1 g, 75%, m.p. 46–48°C, lit. 45–48°C [4]). Anal. Found: C, 49.3; H, 7.2; N, 11.8. $C_{19}H_{32}N_4SSn$ calc.: C, 48.8; H, 6.8; N, 12.0%. ^{1}H NMR: 7.55–7.69 (m, 5H, C_6H_5), 0.85–1.67 (m, 27H, C_4H_9Sn). ^{13}C NMR: 16.41, 28.35, 26.82, 13.46 ($C_{1-4}H_9Sn$), 134.57, 129.32, 123.84, 129.22 ($C_{o,m,p}H_5N$), 155.27 (CN_4).

The following was also prepared by the same method.

(S-Tributylstannyl)-1-methyl-5-thiotetrazole (1). White crystals, yield 43%; m.p. 69–70°C. Anal. Found: C, 41.7; H, 7.7; N, 14.0. $C_{14}H_{30}N_4SSn$ calc.: C, 41.5; H, 7.4; N, 13.8%. ^{1}H NMR: 3.94 (s, 3H, CH_3), 0.85–1.67 (m, 27H, C_4H_9Sn). ^{13}C NMR: 16.28, 28.22, 26.73, 13.46 ($C_{1-4}H_9Sn$), 33.50 (CH_3N), 156.36 (CN_4).

Synthesis of (S-tributylstannyl)-1-phenyl-5-thiotetrazole (3): method 2

A mixture of tributyltin chloride (2.2 g, 11 mmol) and sodium 1-phenyl-5-thiotetrazole (3.58 g, 11 mmol) in ethanol (200 ml) were heated at reflux for 1 h. The mixture was allowed to cool and the solvent removed *in vacuo*. The residue was heated in a hexane/chloroform mixture (10:1) until no further solid would dissolve and the solution filtered. The white product slowly crystallised on cooling (3.78 g, 74%; m.p. 45–47°C). Anal. Found: C, 49.2; H, 7.0; N, 11.9. $C_{19}H_{32}N_4SSn$ calc.: C, 48.8; H, 6.8; N, 12.0%.

The following were also prepared by the same method.

(S-Trimethylstannyl)-1-phenyl-5-thiotetrazole (2). White crystals, yield 67%; m.p. 139–140°C. Anal. Found: C, 35.5; H, 4.1; N, 16.5. $C_{10}H_{14}N_4SSn$ calc.: C, 35.2; H, 4.1; N, 16.4%. ^{1}H NMR: 7.48–7.71 (m, 5H, C_6H_5), 0.80 (s, 9H, CH_3Sn). ^{13}C NMR: −1.92 (CH_3Sn), 134.35, 129.42, 123.84, 129.22 ($C_{o,m,p}H_5N$), 156.34 (CN_4).

(S-Triphenylstannyl)-1-phenyl-5-thiotetrazole (4). Off-white solid, yield 70%; m.p. 126–133°C (lit. 129–137°C [4]). Anal. Found: C, 56.0; H, 3.7; N, 11.1. $C_{25}H_{20}N_4SSn$ calc.: C, 56.9; H, 3.8; N, 10.6%. ^{1}H NMR: 7.38–7.86 (m, 20H, C_6H_5 and C_6H_5Sn). ^{13}C NMR: 137.27, 136.75, 128.96, 130.16 ($C_{o,m,p}H_5Sn$), 134.22, 129.74, 123.61, 129.54 ($C_{o,m,p}H_5N$), 154.18 (CN_4).

(S-Dibutylstannyl)-bis(1-phenyl-5-thiotetrazole) (5). White crystals, yield 58%; m.p. 85–86°C. Anal. Found: C, 45.0; H, 4.7; N, 19.8. $C_{22}H_{28}N_8S_2Sn$ calc.: C, 45.0; H, 4.8; N, 19.1%. ^{1}H NMR: 7.28–7.82 (m, 10H, C_6H_5), 0.86–2.14 (m, 18H, C_4H_9Sn). ^{13}C NMR: 28.15, 27.70, 25.88, 13.46 ($C_{1-4}H_9Sn$), 134.12, 129.45, 122.74, 129.45 ($C_{o,m,p}H_5N$), 155.10 (CN_4).

(S-Diphenylstannyl)-bis(1-phenyl-5-thiotetrazole) (6). White solid, yield 69%; m.p. 209–212°C. Anal. Found: C, 49.7; H, 3.0; N, 17.1. $C_{26}H_{20}N_8S_2Sn$ calc.: C, 49.7; H, 3.2; N, 17.8%. ^{1}H NMR: 7.43–8.12 (m, 20H, C_6H_5 and C_6H_5Sn). ^{13}C NMR: 139.05, 135.38, 129.22, 130.81 ($C_{o,m,p}H_5Sn$), 133.99, 129.64, 122.90, 129.55 ($C_{o,m,p}H_5N$), 153.55 (CN_4).

(S-Dimethylchlorostannyl)-1-phenyl-5-thiotetrazole (7). White solid, yield 52%; m.p. 111–113°C. Anal. Found: C, 30.1; H, 3.0; N, 15.6. $C_9H_{16}ClN_4SSn$ calc.: C, 29.5; H, 4.3; N, 15.3%. ^{1}H NMR: 7.49–7.79 (m, 5H, C_6H_5), 1.35 (s, 6H, CH_3Sn). ^{13}C NMR: 7.72 (CH_3Sn), 133.73, 129.71, 122.54, 129.58 ($C_{o,m,p}H_5N$), 154.75 (CN_4).

The structure of (S-dibutylstannyl)-bis-(1-phenyl-5-thiotetrazole)

Crystal data: $C_{22}H_{28}N_8S_2Sn$, $M = 587.3$, monoclinic, $C2/c$, $a = 14.941(2)$, $b = 9.614(1)$, $c = 19.583(4)$ Å, $\beta = 107.91(2)$, $Z = 4$, $U = 2676.67$ Å^3, $D_c = 1.46$ g cm^{-3}, λ(Mo-K_α) = 0.71069 Å, μ(Mo-K_α) = 10.36 cm^{-1}, $F(000) = 1192$.

Crystals were grown by slow evaporation of a hexane/chloroform (10:1) solution; a crystal of approximate dimensions 0.3 × 0.3 × 0.3 mm was used for data collection. Data were collected in the range $2 < \theta < 22°$ (h 0 → 15, k 0 → 10, l −20 → 20) at room temperature on a Hilger and Watts Y290 automatic four circle diffractometer. Unit cell dimensions were based on 12 centred reflections with $\theta > 15°$. A monitor reflection measured after every 50 reflections showed no systematic decay. In all, 1375 unique observed reflections [$I > 3\sigma(I)$] were collected. Data were corrected for Lorentz and polarisation effects, and also for absorption by an empirical method [23]. The structure was solved by conventional Patterson and Fourier methods [24,25] with the tin sited on the special position

0.5, y, 0.25. Structure factors were taken from the usual sources [26–28]. In the final cycles of refinement all atoms were treated anisotropically, hydrogen atoms being included at calculated positions (C–H, 108 pm) with fixed isotropic temperature factors (0.05 Å^2). Final $R = 7.86\%$ for unit weights and 150 variable parameters, max. shift/e.s.d. = 0.003, residual electron density maxima and minima 0.46, -0.58 e Å^{-3}, respectively.

Final fractional atomic coordinates and isotropic temperature factors are given in Table 3, with selected bond distances and angles in Table 4. The asymmetric unit along with atomic labelling is shown in Fig. 1. A complete table of bond lengths and angles, and lists of thermal parameters and structure factors are available from the authors.

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