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FORMATION OF ORGANOTIN—NITROGEN BONDS

VI* THE INTERMOLECULAR ASSOCIATION OF 2-(TRI-n-BUTYLSTANNYL) TETRAZOLES IN SOLUTION

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Summary

The intermolecular association of 2-(tri-n-butylstannyl)tetrazoles in benzene solution has been evaluated by the measurement of the apparent molecular weight The degree of the association is highly dependent on the steric effect of the 5-substituent of the tetrazoles Low temperature NMR spectra of $CDCl_3$ solutions of 2-(tri-n-butylstannyl) 5-phenyltetrazole and -5-(*p*-nitrophenyl)tetrazole displayed temperature- and concentration dependencies As the temperature decreases, the benzene and tetrazole rings become less coplanar This may be attributed to the closer polymeric association of the 1-nitrogen to tin at low temperature The intermolecular associated form of 2-(tri-n-butylstannyl)tetrazoles in less polar solvents such as benzene and chloroform is confirmed as a 1,3-structure (A)

Introduction

The intermolecular association of *N*-tri-n-butyltin derivatives of imidazole [1], 1,2,4-triazole [1], and 5-substituted tetrazoles [2] in non-polar solution was demonstrated by viscosity measurements In our previous paper [2], the 1,3 structure (A) was proposed for the associated form of the 2-(tri-n-butylstannyl)-5-substituted tetrazoles, and the degree of the association was found to be dependent on the 5-substituent of the tetrazoles

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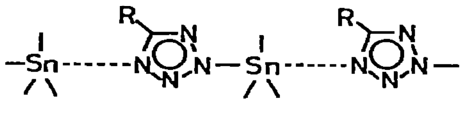
[*] For part V see ref 3



(A)

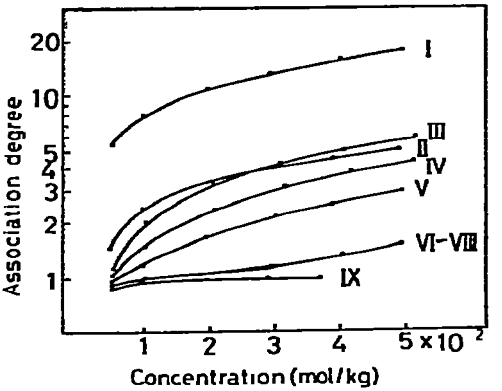
In this paper we present additional results supporting the 1,3-structure (A), and also show that the degree of the association is highly influenced by the steric effect of the 5-substituent rather than the electronic effect.

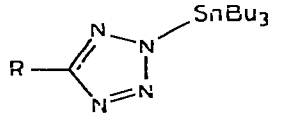
Results and discussion

(a) Apparent molecular weights

The degree of the intermolecular association of 2-(tri-n-butylstannyl)tetrazoles (I-IX) was evaluated by the apparent molecular weights, which were determined by the vapor pressure equilibrium technique. The relations of the apparent molecular weights to the concentrations of the solutions of I-IX are shown in Fig. 1. The degree of the association of compounds I-IX has been found to be influenced by the 5-substituent of the tetrazole in the following order. The 5-substituent = H $\gg$ methyl $\simeq$ *o*-chlorophenyl > *o*-tolyl > *o*-nitrophenyl > phenyl $\simeq$ *p*-tolyl $\simeq$ *p*-anisyl > *p*-nitrophenyl. The much higher degree of association of 2-(tri-n-butylstannyl)-5-unsubstituted tetrazole (I) than the degree of the 5-methyl analogue (II) shows that the steric hindrance of the 5-substituent greatly decreases the degree of the association. This is the reverse of the expected electronic effect, since the methyl group is more electron donating than hydrogen. The electronic effect of the 5-substituent exerts a minor influence on the association compared with the steric effect.

Comparatively higher degrees of the association of 5-(*ortho*-substituted phenyl)tetrazole derivatives (III-V) than the degrees of the 5-phenyl and 5-(*para*-substituted phenyl) analogues (VI-IX) afford an additional confirmation of the predominance of the steric effect over the electronic one. In contrast to the cases of the 5-phenyl and 5-(*p*-substituted phenyl)tetrazole derivatives (VI-IX) in which both the benzene and tetrazole rings lie in the same plane [2], coplanarity of the rings does not appear to occur in the *o*-substituted phenyltetrazole derivatives.



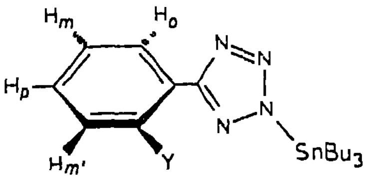


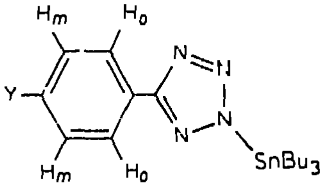
Compound	5-Substituent (R)
I	hydrogen
II	methyl
III	o-chlorophenyl
IV	o-tolyl
V	o-nitrophenyl
VI	phenyl
VII	p-tolyl
VIII	p-anisyl
IX	p-nitrophenyl

Fig. 1. Association degrees of 2-(tri-n-butylstannyl)-5-substituted tetrazoles in benzene solution at 39.2°C

TABLE 1

CHEMICAL SHIFTS OF THE PHENYL PROTONS IN THE NMR SPECTRA OF III-VII AND IX



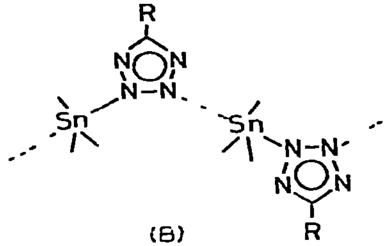


Compound	*o* Substituent	Chem shifts		Compound	*p* Substituent	Chem shifts	
	(Y)	$\delta(H_o)$	$(H_{m,p})$		(Y)	$\delta(H_o)$	$\delta(H_m)$ [$\delta(H_p)$]
III	chloro	7.31	7.31	VI	hydrogen	7.72	7.10[a] (*m*, *p*)
IV	methyl	7.25	7.25	VII	methyl	7.76	7.27[a]
V	nitro	7.5	7.5 (*m*, *p*) 8.0 (*m*′)	IX	nitro	8.31	8.31[a]

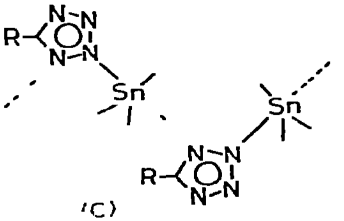
[a] Reported previously in ref. 2.

(III-V) because of the steric hindrance of the *ortho*-substituent The non-coplanarity of the both rings in III-V has been shown by the small anisotropic shifts of the *ortho*-proton of the *o*-substituted phenyltetrazoles in the NMR spectra (Table 1) Compared with the coplanar cases of VI-IX, the non-coplanarity in III-V gives the larger space to the 1-nitrogen of the tetrazole ring This is favorable for the formation of the intermolecular association bond between the 1-nitrogen and tin The higher degree of the association of the 5-(*o*-nitrophenyl)tetrazole derivative (V) than the degree of the 5-phenyltetrazole analogue (VI) also lends strong support to the predominant steric influence of the 5-substituent on the association

The predominant steric effect of the 5 substituent suggests that the 1-nitrogen participates in the intermolecular association So that, among the possible association forms, the 2,3-structure (B) can be excluded, since the steric hindrance of the 5 substituent is considered to be much less effective than the cases of the 1,3-structure (A) and 1,2 structure (C)



(B)



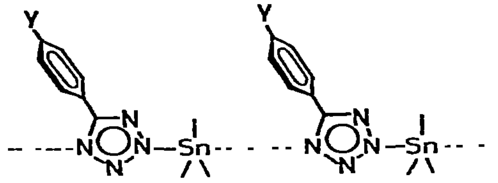
(C)

The 1,2-structure (C) is also improbable, since low association has been found in the cases of *N*-(tri-n-butylstannyl)pyrazole [1] and 2-(tri-n-butylstannyl)-1,2,3-triazoles [3], and since 1,2 dimethyltetrazolium salts could not be produced by the reactions of 2-methyltetrazoles with methyl iodide [4,5] or methyl tosylate [6] The 1,3-structure (A), consequently, is the most probable associated form in non polar solvents

(b) Low temperature NMR spectra

The 1,3 structure (A) has also been confirmed by the low temperature NMR spectra of 2 (tri n butylstannyl) 5 phenyltetrazole (VI) and -5 (*p*-nitrophenyl)-tetrazole (IX) which displayed temperature- and concentration dependencies (Fig 2)

At room temperature, the *ortho*-phenyl protons of VI were deshielded by 0 6-0.7 ppm [$\delta(H_o)$ 8 18, $\delta(H_{m\ p})$ 7 46 ppm in 2 5% $CDCl_3$ solution] due to the tetrazole ring as a result of the coplanarity of the benzene and tetrazole rings [2] At temperatures below −40°C, the band of the phenyl protons became a broad singlet at 7 55 ppm (in 2 5% solution) This implies that the benzene ring is not coplanar with the tetrazole ring below −40°C The non-coplanarity of the two rings could be attributed to the closer intermolecular association of the 1-nitrogen to tin.



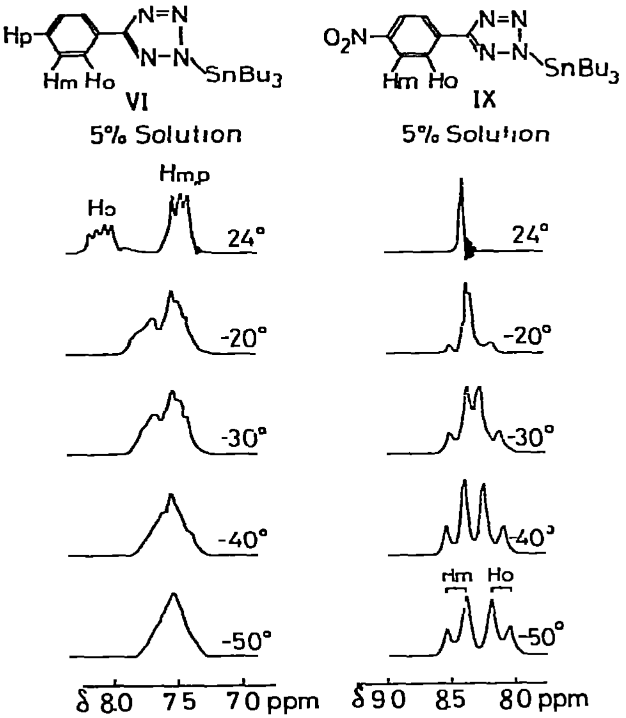


Fig 2 Variable temperature ^{1}H NMR spectra of the phenyl protons of VI and IX

In the NMR spectrum of IX, the four phenyl protons displayed a sharp singlet [$\delta(H_{om})$ 8 38 ppm] at room temperature, because of the equivalent anisotropic effects of the nitro group and the coplanar tetrazole ring [2] As the temperature was lowered to −50°C, the singlet gradually became an AB type quartet [$J(H_{om})$ 9 0 Hz, $\delta(H_o)$ 8 13, $\delta(H_m)$ 8 44 ppm, at −50° in 5% solution] The different anisotropic effect of the tetrazole ring from that of the *p* nitro group suggests that the tetrazole ring becomes less coplanar with the benzene ring at lower temperatures The non-coplanarity of the rings may arise in order to decrease the steric hindrance of the benzene ring for the formation of the intermolecular association bond

In dilute solutions of VI and IX, the spectral change at low temperature is smaller than that in the concentrated solutions This dilution effect strongly supports the proposition that these spectral changes were caused by the closer intermolecular association

There is additional evidence that the NMR spectral change is due to the intermolecular association in the presence of an equimolecular amount of tetrahydrofuran as a ligand in the $CDCl_3$ solution of VI and IX, comparatively smaller changes in the NMR spectra have been observed at lower temperatures (Fig 3) Tetrahydrofuran might behave as a stronger ligand than the 1-nitrogen of the tetrazole ring, breaking the intermolecular association bond between the 1-nitrogen and tin

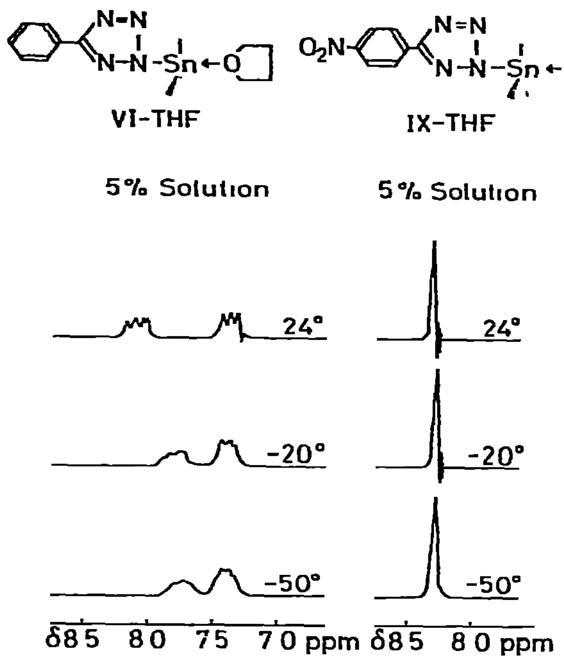


Fig. 3 Variable temperature ^{1}H NMR spectra of the phenyl protons of VI and IX in the presence of an equimolar amount of tetrahydrofuran

No temperature- and concentration-dependencies have been observed in the low temperature NMR spectra of 2-(tri-n-butylstannyl)-5-methyltetrazole (II) and 2-methyl-5-phenyltetrazole (X) In the former case, this might be attributed to the highly associated structure even in a dilute solution (Fig 1). The lack of a spectral change in the latter case indicates that the tri-n-butyltin group is essential for the spectral changes

Experimental

The apparent molecular weight was determined in benzene solution at 39 2°C by the vapor pressure equilibrium technique using Hitachi M-115 apparatus This method is reliable in ±3% range up to molecular weight 2000 from 60 The concentrations of the solutions were varied from 0 005 to 0 05 mol/kg The results are shown in Fig 1

^{1}H-NMR spectra were obtained with JEOL JNM-C60HL spectrometer Chemical shifts are reported in δ units, ppm downfield from internal tetramethyl silane Deuterochloroform was used as a solvent otherwise stated The compounds II and VI-X were prepared as described previously [2,4]

Preparation of 2-(tri-n-butylstannyl)tetrazole (I)

A mixture of 5*H*-tetrazole [7] (0.616 g, 8 80 mmol) and freshly distilled bis(tri-n-butyltin) oxide (2 623 g, 4 40 mmol) was heated in ethanol with refluxing for 30 min. Removal of ethanol in vacuo gave 3 21 g of a pasty liquid of

I NMR ($CDCl_3$) singlet 8 50 ppm (1H, 5-proton), multiplet 0 7-1 7 ppm (27H, n-butyl protons) (Found C, 43 70, H, 8 06, N, 15 59 $C_{13}H_{28}N_4Sn$ calcd C, 43 48, H, 7 86, N, 15 60%)

Preparation of 2-(tri-n-butylstannyl)-5-(o chlorophenyl)tetrazole (III)

A solution of 0 736 g (5 35 mmol) of *o*-chlorobenzonitrile and 1 739 g (5 42 mmol) of tri-n butyltin azide in 5 ml of benzene was heated at 95°C for 7 days in a pressure glass bottle Benzene was distilled off from the reaction mixture to give 2 510 g of crystals which were recrystallized from acetonitrile, m p 123-124°C (Found C, 48 74, H, 6 63 $C_{19}H_{31}ClN_4Sn$ calcd C, 48 59, H, 6 65%)

Preparation of 2-(tri-n-butylstannyl) 5-(o tolyl)tetrazole (IV)

Analogous treatment of an equimolar mixture of *o*-tolunitrile and tri-n-butyltin azide at 100°C for 4 days gave a pasty liquid IV in a quantitative yield On standing for two weeks at room temperature, the liquid began to crystallize very slowly and crystallized completely in several months, m p 102-103°C (acetonitrile) (Found C, 53 30, H, 7 65 $C_{20}H_{34}N_4Sn$ calcd C, 53 48, H, 7 63%)

Preparation of 2-(tri-n butylstannyl)-5 (o nitrophenyl)tetrazole (V)

Analogous treatment of an equimolar mixture of *o* nitrobenzonitrile and tri n butyltin azide at 95°C for 7 days gave pale yellow crystals quantitatively, m p 131-132°C (acetonitrile) (Found C, 47 41, H, 6 38 $C_{19}H_{31}N_5O_2Sn$ calcd C, 47 53, H, 6 51%)

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