^{119}Sn, ^{13}C AND ^{1}H NMR STUDIES OF ARYLOXY- AND ARYLTHIO(1-BUTYL)STANNANES

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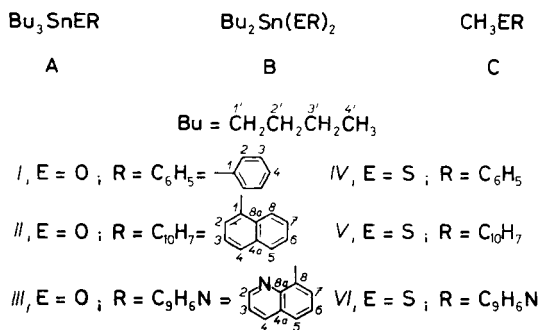*Institute of Chemical Technology, 532 10 Pardubice*

Two series of compounds have been prepared and studied by means of ^{119}Sn, ^{13}C, and ^{1}H NMR spectroscopy, viz aryloxy- and N-heteroaryloxytris(1-butyl)stannanes and their thio analogues Bu$_3$SnER, and diaryloxy- and di(N-heteroaryloxy)bis(1-butyl)stannanes and their thio analogues Bu$_2$Sn(ER)$_2$, where E means oxygen or sulfur, Bu is 1-butyl, R = phenyl, 1-naphthyl, or 8-quinolyl. On the basis of mutual comparison of NMR spectral parameters of both series of organotin compounds and their comparison with NMR spectral parameters of analogous, purely organic compounds CH$_3$ER it is possible to discuss the consequences of the presence of tin atoms in the organotin substituents and of nitrogen heteroatoms in the aromatic systems, and the therefrom following structure of the organotin compounds studied.

In our previous communications[1,2] possibilities were studied of application of multi-nuclear NMR spectroscopy to provide evidence for the presence of and to evaluate the extent of σ–π conjugation in a group of benzyltin compounds; the parameters of ^{13}C and ^{119}Sn NMR spectra were established which are particularly significant for estimation of mutual orientation of the SnCH$_2$ fragment and the plane of aromatic ring and as evidence and measure of hyperconjugative connection between the polarized σ bond Sn—C(H$_2$) and π electron aromatic system. Our continuing interest in structure of organotin compounds, particularly more subtle details of the nature of bonding interactions of the central tin atom and organic substituents and polar groups in simple compounds and with ligands in the corresponding complexes, has led us to the idea of verification of the existence and extent of such a hyper-conjugation in similar organotin compounds having the methylene group of the SnCH$_2$ substituent replaced by an electronegative atom (oxygen or sulfur) with non-bonding electron pair(s), and to the problem of manifestation of this change in the NMR spectra parameters. These problems, closely connected with the mutual orientations of organotin substituent and aromatic nucleus, also immediately affect the possible participation of tin atom in formation of intramolecular bondings (chelate complexes) in such case where the aromatic system contains favourably

situated heteroatoms with free electron pair(s) able to undergo the respective donor--acceptor interaction.

For this purpose we prepared two series of compounds (see Scheme 1), viz. a group of aryloxy- and N-heteroaryloxytris(1-butyl)stannanes and their sulfur analogues Bu_3SnER (A) and a group of diaryloxy- and di(N-heteroaryloxy)bis(1-butyl)stan-

$$Bu_3SnER \qquad Bu_2Sn(ER)_2 \qquad CH_3ER$$

$$A \qquad\qquad B \qquad\qquad C$$

$$Bu = CH_2CH_2CH_2CH_3$$

I, E = O ; R = C_6H_5 =   *IV*, E = S ; R = C_6H_5

II, E = O ; R = $C_{10}H_7$ =   *V*, E = S ; R = $C_{10}H_7$

III, E = O ; R = C_9H_6N =   *VI*, E = S ; R = C_9H_6N

SCHEME 1

nanes and their thio analogues $Bu_2Sn(ER)_2$ (B), where E is an oxygen or sulfur atom, Bu is 1-butyl, and R means phenyl, 1-naphthyl, or 8-quinolyl, and we measured their ^{119}Sn, ^{13}C, and ^1H NMR spectra.

The aim of this present communication is to find the consequences of the presence of tin atom in the organotin substituents and of heteroatoms in the aromatic systems with regard to changes of NMR spectral parameters and to compare these parameters with those of analogous purely organic compounds CH_3ER (C) and thus make corresponding conclusions about structure of the organotin compounds studied.

EXPERIMENTAL

The preparation of compounds *IIA*, *IIIA*, *VIA*, *IIIB*, *VIB* was described in our previous papers[3-6]. Compounds *IB*, *IVB*, *VC* were prepared according to refs[7-9]. Compounds *IA*, *IVA*, *VA*, *VB* were prepared by the procedures used for analogous compounds[8,10]. Table I summarizes the main analytical and physical data of these substances. Compound *IIB* could not be prepared.

The ^1H and ^{13}C NMR spectra were measured with a Bruker AM 400 spectrometer in a 5 mm dual NMR probe at 400·13 and 100·61 MHz, respectively. The chemical shifts $\delta(^1H)$ and $\delta(^{13}C)$ are related to internal tetramethylsilane ($\delta = 0.00$). The samples to be measured were 20% solutions (or saturated solutions, if less soluble) in deuteriochloroform. Temperature 300 K. The one-dimensional (1D) NMR spectra were measured in the standard way with digital resolution of c. 0·2 Hz/point (^1H) or c. 1 Hz/point (^{13}C). The coupling constants $^nJ(^{119}Sn, ^{13}C)$ were determined from the proton-noise decoupled ^{13}C NMR spectra measured with the digital resolution better than 0·2 Hz/point. The two-dimensional (2D) shift-correlated experiments (H,H-COSY, H,C-COSY, H,H,C-RELAY) were carried out with application of the standard

pulse sequences COSY[11], XHCORRDC[11], and RELAY[11]. The selective INEPT spectra were measured according to ref.[12] by means of $^3J(^{13}C, ^1H)$. The NOE difference spectra[13] were measured with the use of the NOEMULT program[11]. The chemical shifts $\delta(^{13}C)$ of compounds IC, IIC, IIIC, and VIC were taken from refs[14-17].

The ^{119}Sn NMR spectra were measured at 37·14 MHz with a JEOL JNM-FX 100 apparatus at 300 K using external tetramethyl stannane as the standard ($\delta = 0.00$).

In all the cases positive values of chemical shifts denote downfield shifts with respect to the standard.

RESULTS AND DISCUSSION

Tables II—IV summarize the ^{119}Sn, ^{13}C, and ^1H NMR spectral parameters of compounds IA—VIA and IB—VIB (Scheme 1). The numbers and intensities of signals fully agree with the formulas given in Scheme 1. The ^{119}Sn, ^{13}C, and ^1H NMR spectral parameters found complement the chemical analyses of the compounds investigated and contribute to their complete identification and characterization.

Univocal assignment of the ^1H and ^{13}C chemical shifts was made on the basis of combination of the one-dimensional (selective INEPT and NOE difference spectroscopy) and two-dimensional (H,H-COSY, H,C-COSY, and H,H,C-RELAY) NMR techniques. At first the proton–proton connectivity was determined by means of homonuclear shift correlated spectra (H,H-COSY). The CH_n connectivity was determined from the heteronuclear shift-correlated spectra (H,C-COSY). The assignment of ^1H chemical shifts of phenyl protons is trivial. The protons in the naphthalene and quinoline derivatives were assigned on the basis of dipolar interaction of the H(4) and H(5) protons in *peri* positions with application of the NOE

TABLE I
Analytical and physical data of the compounds investigated

Compound	Calculated/Found				Boil. temp/Pressure °C/Pa
	% C	% H	% S	% Sn	
IA	56·43	8·42	—	30·98	140—141/60
	55·73	8·40	—	30·4	
IVA	54·15	8·08	8·03	29·74	135—137/60
	54·46	8·34	8·18	29·4	
VA	58·81	7·63	7·14	26·42	160—161/30
	58·66	7·76	7·29	26·1	
VB	60·99	5·85	11·63	21·53	270/35 decomp.
	60·49	5·91	11·86	21·0	

difference spectroscopy. The one-dimensional selective INEPT was used for the assignment of ^{13}C chemical shifts of the quaternary carbon atoms. The proton chemical shifts in 1-butyl groups were assigned from the H,C-COSY spectra in the "inverse" way. The ^{1}H chemical shifts were determined from the known assignment of ^{13}C NMR chemical shifts based on the fact that $^{1}J(^{119}Sn, {}^{13}C) > {}^{3}J(^{119}Sn, {}^{13}C) > {}^{2}J(^{119}Sn, {}^{13}C) > {}^{4}J(^{119}Sn, {}^{13}C)$ (ref.[3]). In the case of compound IIA whose ^{1}H NMR chemical shifts are the same for H(3) and H(4) and very similar for H(6) and H(7) the application of only H,C-COSY spectrum is insufficient for an univocal assignement of the chemical shifts. Therefore, the H,H,C-RELAY technique was used (H(8) → H(7) → C(7); H(5) → H(6) → C(6), and H(2) → H(3) → C(3)).

The ^{1}H NMR spectral parameters (Table II) given in this present paper predominantly serve only for identification of the substances and assignment of the ^{13}C NMR chemical shifts by means of 2D NMR spectra, whereas their contribution to structural and conformational studies of these substances becomes particularly important in the context with the NOE difference experiments which will be dealt with in our next communication.

Shape of Coordination Polyhedrons of Tin Atom

The $\delta(^{119}Sn)$ chemical shift values of compounds IA, IIA, IVA, and VA vary within the limits from 84·1 to 123·7 which is a region typical of four-coordinate tris(1-butyl)

TABLE II
^{1}H NMR chemical shifts of compounds $IA—IIIA$ and $IB—IIIB$ in deuteriochloroform

Compound[a]	$\delta(^{1}H)^{a,b}$										
	2(7)	3(6)	4(5)	5(4)	6(3)	7(2)	8	1′	2′	3′	4′
IA	6·67	7·12	6·73					1·24	1·61	1·32	0·87
IIA	6·55	7·21	7·21	7·68	7·32	7·35	8·26	1·24	1·59	1·28	0·83
$IIIA$	7·09	7·35	7·01	8·00	7·23	8·46		1·15	1·57	1·29	0·84
IVA	7·37	7·13	7·09					1·07	1·49	1·26	0·85
VA	7·71	7·23	7·64	7·73	7·40	7·45	8·55	0·90	1·14	0·90	0·57
VIA	7·91	7·25	7·39	8·02	7·29	8·70		1·11	1·53	1·27	0·80
IB	6·64	7·09	6·77					1·59	1·67	1·25	0·79
$IIIB$	7·23	7·45	6·89	7·85	6·96	8·42		1·13	1·37	1·18	0·69
IVB	7.17	7·43	7·17					1·21	1·41	1·18	0·78
VB	7·74	7·30	7·67	7·79	7·46	7·53	8·72	1·02	1·45	1·22	0·83
VIB	7·94	7·35	7·42	8·21	7·46	8·85		1·49	1·31	1·07	0·50

[a] See Scheme 1; [b] the numbers in parenthesis give the position of hydrogen atoms of the quinoline system.

tin(IV) compounds with tetrahedral or slightly distorted tetrahedral environment of the tin atom[3]. The C—Sn—C bond angles calculated from $^1J(^{119}\text{Sn}, {}^{13}\text{C}(1'))$ values (ref.[18]) for these compounds are ~ 107 to $110°$. The $\delta(^{119}\text{Sn})$ values of compounds *IIIA* and *VIA* show upfield shifts (as compared with those of the isoelectronic compounds *IIA* and *VA*) by 85·5 and 52·9 ppm, respectively, i.e. into a close vicinity of the $\delta(^{119}\text{Sn})$ chemical shifts characteristic of tris(1-butyl)tin(IV) compounds with five-coordinate central tin atom[3]. This fact is a consequence of the interaction of tin

TABLE III

The ^{119}Sn and ^{13}C NMR spectral parameters of the Bu^{n}Sn fragments ($n = 2$ or 3) in compounds *IA—VIA* and *IB—VIB*

Compound[a]	$\delta(^{119}\text{Sn})$	$\delta(^{13}\text{C})/(^nJ(^{119}\text{Sn}, {}^{13}\text{C}))^a$			
		1'	2'	3'	4'
IA	119·1	15·94 (353·6)	27·67 (19·9)	26·95 (63·0)	13·47 *b*
IIA	123·7	16·12 (352·4)	27·69 (20·5)	26·91 (62·1)	13·54
IIIA	38·2[c]	19·93 (390·2)	28·11 (17·9)	27·09 (66·9)	13·54
IVA	84·1	14·28 (326·4)	28·43 (21·5)	26·93 (62·6)	13·50
VA	89·1	14·43 (323·7)	28·35 (21·4)	26·88 (62·0)	13·42 *b*
VIA[d]	36·2	17·92 (355·1)	28·60 (20·5)	26·90 (65·7)	13·40
IB	−115·0	22·36 (523·4)	26·76 (25·0)	26·59 (90·0)	13·12 *b*
IIIB[e]	−260·0	25·46 (612·8)	27·73 (25·6)	26·75 (105·0)	13·50 *f*
IVB	112·0	18·90 (367·2)	27·82 (25·6)	26·41 (74·9)	13·36 *b*
VB	115·2	19·39 (358·7)	27·66 (25·6)	26·33 (76·8)	13·13 *b*
VIB[d]	−145·4	29·48 (635·9)	27·98 (39·2)	26·00 (111·8)	13·27 (5·6)

^{a} See Scheme 1; ^{b} less than 5 Hz; ^{c} ref.[3]; ^{d} ref.[5]; ^{e} ref.[6]; ^{f} less than 10 Hz.

TABLE IV
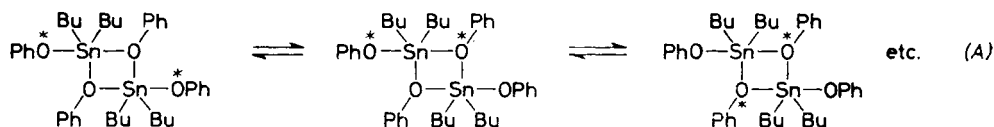
The ^{13}C chemical shifts (Hz) and $^nJ(^{119}Sn, ^{13}C)$ coupling constants of the substituents R in compounds $IA-VIA$ and $IB-VIB$ in deuterio chloroform

Compound[a]	$\delta(^{13}C)^a/(^nJ(^{119}Sn, ^{13}C))^{a,b}$									
	1(8)	2(7)	3(6)	4(5)	4a	8a	5(4)	6(3)	7(2)	8
IA	162·05 (25·2)	119·61 c	129·17 (12·7)	118·31 c						
IIA	158·52 (27·6)	111·21 (14·8)	126·21 c	117·72 c	135·18 c	128·98 (10·2)	127·30 c	125·58 c	123·88 c	123·00 c
IIIA	157·82 (31·3)	113·97 (16·6)	128·87 c	113·80 c	129·26 c	139·98 c	136·69 c	120·79 c	143·78 c	
IVA	134·95 (20·0)	134·63 (9·8)	128·35 (4·3)	125·52 (5·3)						
VA	132·99 (21·8)	133·53 (11·9)	125·14 (5·9)	126·70 (6·7)	134·04 (4·4)	136·01 (6·0)	128·16 c	125·76 c	125·76 c	127·76 c
VIA	139·09 (8·6)	131·02 (15·7)	126·35 c	123·17 c	128·73 (3·4)	145·16 (5·6)	137·19 c	120·72 (2·8)	146·74	
IB	159·42 d	120·35 d	129·21 c	119·87 d						
IIIB	158·19 (27·1)	113·29 (11·9)	130·03 c	112·36 c	129·56 (9·3)	136·63 (33·2)	138·04 c	120·75 c	142·20 (4·6)	
IVB	132·63 (23·3)	134·87 (13·0)	128·64 (5·7)	126·41 (7·4)						
VB	130·71 (25·4)	134·05 (16·0)	125·28 (8·0)	127·57 (8·2)	134·08 (5·6)	135·83 (8·2)	128·28 c	125·99 c	126·22 c	127·07 c
VIB	142·48 (12·5)	130·82 (7·3)	127·38 c	121·97 c	129·30 (6·0)	144·97 (5·4)	138·41 c	120·99 (3·4)	145·91 c	

[a] See Scheme 1; [b] the numbers in parenthesis give the position of carbon atoms in quinoline system; [c] $^nJ(^{119}Sn, ^{13}C) < 4$ Hz; [d] broadened signals due to exchange.

atoms with nitrogen heteroatoms of 8-quinolinolate or 8-quinolinethiolate (oxinate or thiooxinate) ligand i.e. of the formation of chelate complexes with distorted *cis*-trigonal bipyramidal arrangement (the average C—Sn—C angles according to ref.[18] are ~114° and 110°, the theoretical angle is 100°).

According to the value $\delta(^{119}Sn) = -115\cdot0$, which is typical of five-coordinate bis(1-butyl)tin(IV) compounds, the substance *IB* dissolved in deuteriochloroform represents a dimer containing the Sn_2O_2 fragment, which is usual with compounds of the $R_2Sn(OR')_2$ type[19]. This fact does not contradict the finding that only one set of signals for OPh groups was observed in the ^{13}C NMR spectra of this compound. The signals of carbon atoms C(1), C(2), and C(4) are considerably broadened and their half-widths decreased with increasing temperature, which can be ascribed to the dynamic equilibrium in the NMR time scale in the sense of Eq. (*A*).

$$\begin{array}{ccc}
\overset{*}{\text{Bu}}\ \text{Bu}\ \text{Ph} & \text{Bu}\ \overset{*}{\text{Bu}}\ \text{Ph} & \text{Bu}\ \text{Bu}\ \overset{*}{\text{Ph}} \\
\text{PhO}-\text{Sn}-\text{O} & \text{PhO}-\text{Sn}-\text{O} & \text{PhO}-\text{Sn}-\text{O} \\
\text{O}-\text{Sn}-\overset{*}{\text{OPh}} & \text{O}-\text{Sn}-\text{OPh} & \text{O}-\text{Sn}-\text{OPh} \\
\text{Ph}\ \text{Bu}\ \text{Bu} & \text{Ph}\ \text{Bu}\ \text{Bu} & \text{Ph}\ \text{Bu}\ \text{Bu}
\end{array} \qquad \text{etc.} \qquad (A)$$

The system of such dimeric units can best be described as a set of two distorted trigonal bipyramides connected with each other by a common edge formed by two oxygen atoms. The extent of deformation can be visualized by the magnitude of average C—Sn—C bond angles which are c. 126° in compound *IB* (ref.[18]). The other compounds with phenoxy or phenylthio groups, *IA*, *IVA*, and *IVB*, which are monomeric (vide infra), gave very narrow signals in their ^{13}C NMR spectra, so it was possible to determine the coupling constants $^nJ(^{119}Sn, ^{13}C)$, too.

In contrast to the compounds with Sn—O bond, those with Sn—S bond are not able of dimerization, hence compounds *IVB* and *VB* in deuteriochloroform solutions exist as simple monomers, almost ideal tetrahedral molecules. This fact is manifested by the values of their $\delta(^{119}Sn)$ chemical shifts typical of four-coordinate bis(1-butyl) tin(IV) compounds[6] and by the values of the coupling constants $^1J(^{119}Sn, ^{13}C)$ and the therefrom determined magnitudes of the C—Sn—C bond angles ~111° and 110°, respectively. The compounds *IIIB* and *VIB* are chelate complexes with trapezoidal-bipyramidal (skew) arrangement (the C—Sn—C bond angles ~135° and 138°, respectively) of the environment of the central (six-coordinate) tin atom[6]. A more detailed description of structure of the chelate compounds *IIIA*, *IIIB*, *VIA*, and *VIB* based on the analysis of their ^1H, ^{13}C, ^{15}N, and ^{119}Sn NMR spectral parameters is presented elsewhere[5,20]. However, the increased coordination of tin atom in these complexes is indicated also by the values of $\delta(^{13}C)$ chemical shifts of C(1') atoms (Table III) which all show a distinct downfield shift (by c. 3 to 10 ppm) as compared with the four-coordinate compounds[3,6].

Mutual Orientation of Aromatic Substituents R *and the Rest of Molecules*

Aromatic alkyl phenyl ethers C_6H_5OR (inclusive of compound *IC*) whose R substituents are not too bulky exist in the form of planar conformers[21] both in solution and as neat substances, which is a consequence of the interaction of non-bonding electron pairs of oxygen atom with the π electronic system of phenyl nucleus (the p–π conjugation). Such arrangement makes itself felt in a characteristic way also in the ^{13}C NMR spectra of the compounds. The chemical shifts $\delta(^{13}C(1))$ (see Scheme 1) assume the values of ~ 160 ppm or higher (i.e. they are distinctly shifted to lower field as compared with $\delta(^{13}C)$ of benzene $(128\cdot5$ ppm$)[22]$), whereas the $\delta(^{13}C(4))$ values — on the contrary — show upfield shifts (~ 120 ppm or less)[21]. The $\delta(^{13}C)$ values of both relevant carbon atoms of compound *IA* lie in a region typical of planar arrangement and, hence, do not differ in structure and its ^{13}C NMR spectral manifestations from the organic ethers C_6H_5OR in which R = methyl, ethyl, 1-propyl, or 2-propyl and from analogous organotin(IV) phenoxides $C_6H_5OSnR_3$ (R = = methyl or ethyl), but they do differ markedly from compound $C_6H_5OC(CH_3)_3$ whose molecule is not planar due to steric effects[21]. The Bu_3SnO substituent, whose Sn—O bond is longer than C—O bond, does not interfere with the planar arrangement of the Sn—O—C_6H_5 fragment, and this is eventually obvious from the downfield shift of $\delta(^{13}C(2))$ values of compound *IA* (as compared with *IC*) (reduction of γ-effect, lowering of steric interactions)[23]. The values of $\delta(^{13}C(1))$, $\delta(^{13}C(2))$, and $\delta(^{13}C(4))$ parameters indicate that the conformation with planar C_6H_5OSn fragments predominates also in the dimeric compound *IB*.

The share of planar conformers in compounds RSC_6H_5 markedly decreases with the chain length of R substituents (R = H, CH_3, C_2H_5, 1-C_4H_9), being c. 10% in compound $CH_3SC_6H_5$ (*IVC*)[24,25]. Increasing share of the non-planar conformer causes upfield shift of $\delta(^{13}C(1))$ value and downfield shifts of $\delta(^{13}C(2))$ and $\delta(^{13}C(4))$ values[25]. In the same sense and even more markedly shifted are the $\delta(^{13}C)$ values of C(1), C(2), and C(4) carbon atoms in compounds *IVA* and *IVB* as compared with the respective ^{13}C NMR parameters of compound *IVC*, whereby they distinctly differ from their oxygen analogues.

The conformational differences between compounds *IA* and *IB* on the one hand and between *IVA* and *IVB* on the other hand are also reflected in the long-range coupling constants $^nJ(^{119}SnOC(1-4))$ and $^nJ(^{119}SnSC(1n-4))$, respectively, where $n = 2-5$. The order of $^nJ(^{119}SnSC(1-4))$ values of compounds *IVA* and *IVB* is typical of the non-planar arrangment of phenyl ring and substituents Bu_3SnS— and $Bu_2Sn(SC_6H_5)S$—, respectively, which is found, e.g.,in benzyltin(IV) compounds[1,2,26] (first of all it is significant that $^5J > {}^4J$) with distinct σ–π conjugation of the polarized bond Sn—C and phenyl nucleus; the order of $^nJ(^{119}SnOC(1-4))$ values of compounds *IA* and *IB* is substantially different, and the values $^4J > {}^5J$ (if they were measurable at all). Hence it can be stated that in compounds

IA, IB, IC the fragments $SnOC_6H_5$ are predominantly planar, whereas in their thio-analogues *IVA, IVB, IVC* the conformers with non-planar $SnSC_6H_5$ fragments are present or even predominant. The prevailing share of non-planar conformer with participation of the $\sigma–\pi$ conjugation in compound $Me_3SnSC_6H_5$ could recently be proved by Cauletti et al.[27] using the photoelectron spectra. Certain similarities in structure and ^{119}Sn NMR spectra of compounds with $SnSC_6H_5$ and $SnCH_2C_6H_5$ groupings were found recently by Harris and Sebald[28].

In accordance with expectation, the effect of CH_3O substituent on $\delta(^{13}C)$ chemical shifts of the carbon atoms at equivalent positions of benzene, naphthalene, and quinoline will make itself felt (Table V) in similar values of ^{13}C SCS. The upfield shift of ^{13}C SCS values of carbon atoms at *ipso* positions $(C(1)$ or $C(8))$ in the series *IC, IIC, IIIC* is in accordance with the general effect of substituent at the position of substitution[16]. The average values of ^{13}C SCS of carbon atoms at formally *ortho* positions $(C(2)$ and $C(8a)$ for compound *IIC* equal to $-14\cdot9$ ppm, $C(7)$ and $C(8a)$ for compound *IIIC* equal to $-14\cdot4$ ppm) are identical with or very close to the same value of compound *IC* $(-14\cdot4$ ppm). The ^{13}C SCS values of formally *para* positions (the positions 4, 4, and 5 in compounds *IC, IIC*, and *IIIC*, respectively) differ but sligthly $(0\cdot1$ ppm)[16]. All these facts confirm that all three compounds dissolved in deuteriochloroform exist predominantly in the form of planar conformers. The ^{13}C SCS values of $C(2)$ in compound *IIC* and $C(7)$ in *IIIC* show distinct upfield shifts as compared with those of $C(8a)$, which is due (i) to the higher negative charge induced at this position by the mesomeric effect of CH_3O substituent (the negative charge at $C(8a)$ carbon atom is lower due to "instability" of the corresponding mesomeric structure)[29] and (ii) to greater shielding of $C(2)$ and $C(7)$ carbon atoms caused by the polarization of $C(2)$—H and $C(7)$—H bonds, respectively, as a consequence of the steric interferences of hydrogen atoms of these bonds with hydrogen atoms of the CH_3O substituent in the predominating *E*-conformers of the compounds[16] (Scheme 2).

The substituent Bu_3SnO causes practically the same chemical shifts $\delta(^{13}C)$ of carbon atoms at equivalent positions of benzene and naphthalene but distinctly

conformer *E*   conformer *Z*

X = CH or N ; R' = CH_3,Bu_3Sn or $Bu_2Sn(ER)$; E = O or S
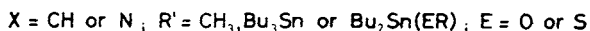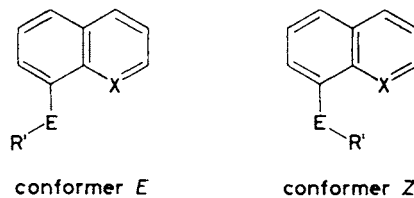
SCHEME 2

TABLE V

The ^{13}C SCS values of compounds $IA-VIA$, $IB-VIB$, and $IC-VIC$ in deuteriochloroform

Compound[a]	^{13}C SCS[b,c]									
	1(8)	2(7)	3(6)	4(5)	4a	8a	5(4)	6(3)	7(2)	8
IA	33·55	−8·89	0·67	−10·19						
IB	30·92	−8·15	0·71	−8·63						
IC	31·4	−14·4	1·0	−7·7						
IIA	30·82	−14·39	0·61	−9·98	1·88	−4·38	−0·40	−0·02	−1·72	−4·7
IIC	27·6	−22·0	−0·1	−7·6	1·0	−7·8	−0·40	+0·6	−0·6	−5·8
IIIA	28·42	−15·43	2·37	−13·9	0·96	−8·32	0·69	−0·21	−6·58	
IIIB	28·79	−16·11	2·33	−15·34	1·26	−11·63	2·04	−0·25	−8·1	
IIIC	26·5	−21·2	0·7	−7·7	1·40	−7·6	0·2	−0·9	−0·9	
IVA	6·45	6·13	−0·15	−2·98						
IVB	4·13	6·37	0·14	−2·09						
IVC	9·9	−1·9	0·1	−3·1						
VA	5·29	7·93	−0·46	−1·00	0·74	2·71	0·46	0·16	0·16	0·06
VB	3·01	8·45	−0·32	−0·13	0·78	2·53	0·58	0·39	0·62	−0·63
VC	8·9	−1·82	−0·02	−1·9	0·30	−1·60	0·74	0·51	0·43	−3·44
VIA	9·69	1·62	−0·15	−4·53	0·43	−3·14	1·19	−0·28	−3·56	
VIB	13·08	1·42	0·88	−5·73	1·00	−3·33	2·41	−0·01	−4·39	
VIC	11·1	−6·2	0·7	−3·8	0·2	−2·5	0·7	1·2	−0·9	

[a] See Scheme 1. [b] The numbers in parenthesis denote the positions in quinoline. [c] The SCS values are defined as differences of $\delta(^{13}$C) values, of individual carbon atoms in the compounds studied and $\delta(^{13}$C) values of the corresponding carbon atoms of benzene[21], naphthalene[23] and quinoline[16].

different shifts in the corresponding positions of quinoline (the ^{13}C SCS of C(4) atoms are: -10.19 ppm (*IA*), -9.98 ppm (*IIA*), but -13.9 ppm (*IIIA*); ^{13}C SCS of C(2) atom in *IA* is -8.99 ppm, the average value of ^{13}C SCS of C(2) and C(8a) in *IIA* is -9.38 ppm, but the average value of ^{13}C SCS of C(7) and C(8a) in *IIIA* is -13.87 ppm). The higher resonance donor ability of R_3SnO substituent (as compared with that of $CH_3O)^{30}$ results in downfield shifts of the ^{13}C SCS values of C(1) in compounds *IA* and *IIA* as compared with the corresponding values in *IC* and *IIC*, whereas the same reason causes upfield shifts of the ^{13}C SCS values of C(4) atoms[31]. The distinct downfield shift of ^{13}C SCS values of C(2) atoms in compounds *IA* and *IIA* as compared with *IC* and *IIC* is obviously connected with the lowered sterical interferences of H(2) hydrogen atoms with the much more distant hydrogen atoms of Bu_3SnO substituent.

The different effect of Bu_3SnO substituent on the ^{13}C NMR spectral parameters of equivalent positions in naphthalene and quinoline predominantly consists in upfield shifts of all ^{13}C SCS of carbon atoms in resonance positions of compound *IIIA* as compared with *IIA*. The increased donor ability of substituent in this case is caused by the increase of overall electron density at the central tin atom due to formation of the donor–acceptor bond $Sn \rightarrow N$ (refs[1,2]). In compound *IIIB* the donor abilities of substituent are still more emphasized due to formation of two donor––acceptor $Sn \rightarrow N$ bonds (another upfield shift of resonance positions of quinoline system) in contrast to compound *IB* in which the substituent of phenyl ring (i.e. the rest of the molecule, $Bu_2Sn(OC_6H_5)O)$ is a wekaer donor than the Bu_3SnO substituent in compound *IA* because of the presence of the electronegative OC_6H_5 group, and partially also because of the withdrawal of electron density from oxygen atoms due to formation of the donor–acceptor connection $Sn \rightarrow O$ during formation of the dimer of this compound (vide supra). Another significant difference consists in the fact that, whereas in compound *IIIA* (and also *IIIB*) the ^{13}C SCS value of C(8a) atom is shifted upfield as compared with that in compound *IIIC*, the opposite relation holds for the same parameters in the pair *IIA* and *IIC*. In our opinion this fact is caused not only by the formation of donor–acceptor $Sn \rightarrow N$ bond in compound *IIIA* (or also *IIIB*) but also by different conformations of compounds *IIA* and *IIIA*. According to all indications, the compound *IIA* is the *E*-conformer, the compound *IIIA* (and the respective fragments of compound *IIIB*) must necessarily be the "Z-conformer" (formation of chelates). In compound *IIIB* the relatively higher strength of donor–acceptor connection and electron-donor action of the organotin(IV) substituent on the aromatic system will make themselves felt by a distinct (long-range) spin–spin coupling between the tin atom and some carbon atoms of the N-heteroaromatic section of the quinoline substituent (Table IV).

The effect of CH_3S substituent at the ^{13}C SCS-equivalent positions of benzene, naphthalene, and quinoline is far less univocal than that of CH_3O. A significant role is played here obviously by different proportions of planar and non-planar conformers

of the individual compounds. From the ^{13}C SCS calues of $C(2)$, $C(4)$, and $C(8a)$ atoms we can clearly see the share of non-planar conformers in compounds *IVC* and *VC*, whereas compound *VIC* shows all indications of the „planar E-conformer"[16]. Replacement of CH_3S substituent by Bu_3SnS (compounds *IVA* and *VA* and *VIA*) will make itself felt on the atom bearing the substituent ($C(1)$ or $C(8)$) by an upfield shift of ^{13}C SCS values, and on the atoms at formal *para* positions (except for compound *VIC*) — on the contrary — by a downfield shift; the opposite was true for the oxygen-containing substituents. The above-mentioned replacement will also distinctly affect the formal *ortho* positions (particularly $C(2)$ or $C(7)$ atoms). The logical origin of all these changes lies in the structure of these compounds. Obviously the share of non-planar conformers of compounds *IVA* and *VA* is higher than that of compounds *IVC* and *VC*, which also affects the donor ability of substituents ($CH_3S > Bu_3SnS$) and the type of cojugative connection (the $p–\pi$ conjugation of the predominant planar conformers of compounds *IVC* and *VC* is transformed into $\sigma–\pi$ conjugation of the polarized Sn—S bond with the aromatic π system of compounds *IVA* and *VA*). The distinct differences of ^{13}C SCS of formal *ortho* positions (mainly the $C(2)$ atom) of compounds *IVA* and *VA* on the one hand and *IVC* and *VC* on the other hand, which are a consequence of decreased sterical interaction between $H(2)$ and hydrogen atoms of the substituent, do not contradict the above-mentioned conclusion. The predominant share of non-planar conformers of compounds *IVA* and *VA* and, moreover, of compounds *IVB* and *VB* is also supported by the order of the long-range coupling constants $^nJ(^{119}SnS, ^{13}C)$ in Table V. In all the cases it is $^5J > {^4J}$. The replacement of the substituent Bu_3SnS by $Bu_3Sn(SR)S$ will make itself felt in the values of ^{13}C SCS of pairs of compounds *IVA*, *IVB* and *VA*, *VB* identically with the respective effect on their oxygen analogues.

The relative changes of relevant ^{13}C SCS of compounds *VIA*, *VIB* as compared with compound *VIC* are of the same kind as those discussed in the case of their oxygen analogues. This is also evidence for the conformation change $E(VIC) \rightarrow$ $\rightarrow Z(VIA$ or *VIB*) as a necessary condition of formation of intramolecular bonding connection $Sn \rightarrow N$ in chelate complexes of compounds *VIA* or *VIB*.

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