Conformational Studies of Dithiastannolanes by Dynamic Nuclear Magnetic Resonance Spectroscopy

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The barriers to conformational interconversion of the five-membered rings of the title compounds of general type $SnRR'(SCH_2CHR''S)$ (R, R' = Me or Ph; R'' = H or Me) have been measured for the first time by low-temperature n.m.r. studies. Room-temperature measurements indicate that the chelate rings exist as half-chair conformations with the $-CH_2CHR''-$ moiety in a fully staggered configuration, as in the solid state. These findings are at variance with a previous n.m.r. study of this type of system. The $\Delta G^{\ddagger}$ values for the interconversion of the two half-chair conformations lie in the range 30—32 kJ mol^{-1} and are essentially independent of the substituents on the Sn^{IV} atom and on the five-membered ring.

As part of a wider study of the dynamic properties of main-group and transition-metal compounds containing open-chain, chelating, and bridging sulphur ligands, we have isolated the organotin sulphides $SnRR'(SCH_2CHR''S)$ (R,R' = Me or Ph; R'' = H or Me). Although this type of compound has been prepared previously,[1] earlier structural studies involving Mössbauer,[2] ^1H and ^{119}Sn n.m.r.,[2,3] and u.v. photoelectron spectroscopic[3,4] techniques have been based on an assumed tetrahedral four-co-ordination of Sn and have supported a C_s symmetry of the ring. However, a recent X-ray study[5] of $SnMe_2(SCH_2CH_2S)$ clearly revealed a trigonal-bipyramidal five-co-ordination of Sn with the molecules arranged in a chain in the crystal, and the five-membered rings adopting a chiral puckered conformation.

We now report on detailed low-temperature n.m.r. studies of these compounds, which establish that the stereodynamics of the five-membered ring are fully compatible with the solid-state crystal structure. They also establish that the previous variable-temperature n.m.r. studies[3] on some of these compounds were incorrect both in terms of experimental observation and spectral interpretations.

Experimental

Preparations.—Dimethyl- and diphenyl-tin dichlorides were prepared by standard methods.[6] Methyl(phenyl)tin dichloride was prepared as previously.[7] Ethane-1,2-dithiol and propane-1,2-dithiol were used as supplied. All five dithiacyclopentane derivatives of $SnMe_2Cl_2$ were prepared in a manner similar to that previously reported,[1] $SnMePh(SCH_2CH_2S)$ (m.p. 107 °C) and $SnMePh(SCH_2CHMeS)$ (liquid at room temperature) being new compounds.

Spectra.—Proton n.m.r. spectra were initially recorded at 100 MHz on a JEOL PS/PFT-100 spectrometer using a standard variable-temperature probe. The compounds were dissolved in a CD_2Cl_2–CS_2 solvent mixture in most cases and spectra recorded down to the low-temperature limit of this instrument, ca. −115 °C. At this temperature, bands characteristic of individual conformers (see below) were partially but not fully revealed. We therefore resorted to the 400-MHz facilities at the University of Warwick to take advantage of (i) the larger chemical shift dispersion of this instrument and its consequently greater effectiveness in 'freezing out' the conformational interconversion, and (ii) its slightly lower accessible probe temperatures compared to our 100-MHz instrument. Band-shape analyses were performed using the authors' modified version of the DNMR program of Kleier and Binsch.[8]

Results

Spectral Observations.—A preliminary examination of the variable-temperature spectra of the compounds $SnMe_2$-(SCH_2CH_2S), $SnMePh(SCH_2CH_2S)$, and $SnMe_2(SCH_2CH-MeS)$ revealed no significant changes in the methyl, methylene, or methine signals in the range +50 to −50 °C. We studied particularly closely the compound $SnMe_2(SCH_2CHMeS)$ since it had been reported[3] that the methyltin signal changed from three lines at +50 °C to two lines at −45 °C. No such change was observed even when using the same solvent ($CDCl_3$) as previously,[3] and it is our opinion that the previously observed changes were artifacts arising from the variation of magnetic field homogeneity with temperature. We are also unable to accept the authors' explanations of their observations since individual conformers (such as the *gauche* forms A and B they depict, Figure 2 of ref. 3) would be rapidly interconverting at all temperatures between −45 and 50 °C and therefore not separately detectable (see later).

The 400-MHz variable-temperature ^1H spectra of the compounds will now be described in turn.

$SnMe_2(SCH_2CH_2S)$. The ambient-temperature spectrum simply consisted of a single band (plus ^{117}Sn, ^{119}Sn satellites) due to the methyltin protons and a single sharp band (plus tin satellites) due to the four methylene protons. On cooling, the methylene signal commenced broadening from ca. −80 °C onwards. At −120 °C the breadth of the band ($\Delta\nu_{\frac{1}{2}}$) was 260 Hz (0.65 p.p.m.), but by −125 °C the band had split into a broad doublet ($\Delta\nu_{\frac{1}{2}} \approx 240$ Hz). No splitting was observed in the methyltin signal although at this lowest temperature its band width had increased to 22 Hz. Chemical shift and coupling-constant data are reported in Tables 1 and 2.

$SnPh_2(SCH_2CH_2S)$. The variable-temperature spectra of this compound were very similar to those of $SnMe_2(SCH_2-CH_2S)$, the main difference being that, due to solubility problems, it proved impossible to cool the sample below ca. −100 °C. By this temperature a very broad $-CH_2-$ band was detected but the ring conformational process had not been slowed sufficiently for the static conformers to be detected. No energy-barrier calculations were therefore possible.

$SnMe_2(SCH_2CHMeS)$. The 100-MHz room-temperature spectrum could be interpreted on the basis of an $ABCX_3$ spin system for the protons on the sulphur ligand. The methyltin protons showed as two lines as a result of the non-equivalence induced by the ring methyl group. At 400 MHz the ligand proton spectra could be interpreted on a first-order basis and data are listed in Tables 1 and 2. All the bands with the exception of $-CMe$ showed tin satellites. The assignment of the geminal $-CH_2-$ protons was based both on the assumption that the more highly shielded proton would be that *cis* to CH_3,

Table 1. ^{1}H Chemical shifts (δ/p.p.m.) of dithiastannolanes

Compound	θ_c/°C	$-CH_2-$		$\rangle CH-$	CH_3-C	CH_3-Sn		$Ph-$
SnMe$_2$(SCH$_2$CH$_2$S)	a	3.06				0.87		
	−125	2.46	3.46			ca. 0.87 ^{b}		
SnMePh(SCH$_2$CH$_2$S)	a	3.08				1.01		7.24—7.63
	−120	2.62	3.34			ca. 1.01 ^{b}		7.24—7.63
SnPh$_2$(SCH$_2$CH$_2$S)	a	3.20						7.20—7.85
	−120	ca. 3.17 (vbr)						7.20—7.85
SnMe$_2$(SCH$_2$CHMeS)	a	2.84	3.17	3.54	1.43	0.85	0.88	
	−125	$\{$ 2.34 ^{c}	3.28 ^{c}	3.04 ^{c}	1.41 ^{c}			
		3.30	2.79	4.00	1.18	0.85 ^{b}	0.88 ^{b}	
SnMePh(SCH$_2$CHMeS)	a	$\{$ 2.94	3.29	ca. 3.66	1.52	1.09		
		2.96	3.31		1.53	1.12		7.25—7.88
	−110	Very broad, complex envelope			ca. 1.53 ^{b}	ca. 1.1 ^{b}		7.25—7.88

^{a} Room temperature (ca. 28 °C). ^{b} Band broadened but not split. ^{c} More abundant (58%) isomer.

Table 2. Spin-spin coupling constants (J/Hz) for dithiastannolanes

Compound	$^2J_{gem}$	$^3J_{cis}$	$^3J_{trans}$	$^3J(CH_3,H)$	$^2J(^{117}Sn,{}^{119}Sn-H)$	$^3J(^{117}Sn,{}^{119}Sn-H)$
SnMe$_2$(SCH$_2$CH$_2$S)	a	a	a		59.0, 61.0	43.3, 44.8
SnMePh(SCH$_2$CH$_2$S)	b	b	b		59.9, 62.6	44.7, 46.5
SnPh$_2$(SCH$_2$CH$_2$S)	a	a	a			ca. 45.5 ^{c}
SnMe$_2$(SCH$_2$CHMeS)	−12.45	3.01	7.56	6.76	59.0, 61.8	39.6, 40.8 (Sn-H$_{A,D}$)
						54.0, 56.4 (Sn-H$_{C,F}$)
SnMePh(SCH$_2$CHMeS)	−12.38	3.11	7.67	6.77	d	d

$^{a(b)}$ Not measurable from ^{1}H spectra on account of exact (apparent) chemical shift equivalence of methylene protons at ambient temperatures. ^{c} Approximate average ^{117}Sn,^{119}Sn-H value. ^{d} Not measured due to complexity of satellite spectrum.
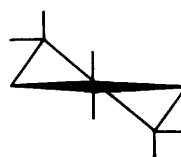
and also on the vicinal coupling constant/dihedral angle predictions of the Karplus theory.[9] The spectra remained unchanged in the temperature range 50 to −50 °C, in contrast to the previous report.[3] However, below ca. −80 °C, the ring proton bands started to broaden appreciably (Figure 1). The broadenings continued with further reduction in temperature. Below ca. −110 °C additional bands were observed which then proceeded to sharpen with further decrease in temperature. At the lowest temperature, −125 °C, five bands were detected (Figure 1). The relative intensities, however, suggested that there was an overlapping of two bands. The spectral changes therefore indicate that in this compound at −125 °C two distinct conformers are distinguishable, but these have not been fully ' frozen out ' since the bands are still somewhat broad ($\Delta v_{\frac{1}{2}} \approx$ 40 Hz). As a consequence no indirect spin–spin couplings were detectable. The relationship between the room- and low-temperature spectra is shown in Figure 2. The two conformers exist in relative abundancies of ca. 3 : 2. The lowest temperature spectrum is notable for the very large differences in chemical shift for corresponding ring protons in the two conformers. A similar splitting of the CH$_3$-Sn signal was observed in the same temperature range although the magnitude of this conformer splitting was smaller than in the methylene region (Table 1).

SnMePh(SCH$_2$CH$_2$S). The ambient-temperature spectrum of this compound is notable in that only a single ring methylene signal was observed at both 100 and 400 MHz. This is unexpected since even for a pseudo-planar ring two signals are expected by virtue of the absence of a C_2 axis of symmetry. The methyltin protons also showed as a sharp singlet and the phenyl region was predictably complex. On cooling, the methylene region commenced broadening at ca. −80 °C and by −120 °C two broad bands were seen, rather analogous to those observed for SnMe$_2$(SCH$_2$CH$_2$S). No major changes were observed in the methyltin signal apart from some broadening.

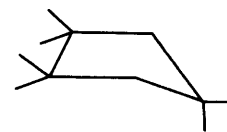SnMePh(SCH$_2$CHMeS). In this case, room-temperature spectra are reported in both CDCl$_3$ and C$_6$D$_6$ solvents since certain differences were noted. In CDCl$_3$ two methyltin singlets and two C-methyl doublets were observed with approximately equal intensities, indicating that two structural isomers of the compound existed. The methylene region showing as the ABC portions of two ABCX$_3$ systems at 100 MHz and two first-order three-spin systems at 400 MHz similarly exemplified this. The ^{1}H chemical shift distinctions between these structural isomers were relatively small ($\leqslant$0.02 p.p.m.). Indeed, in C$_6$D$_6$ solvent no isomer distinction was seen in the methyltin signal. Therefore, in order to establish more firmly the presence of these two isomers a 74.5-MHz ^{119}Sn spectrum was obtained. In the presence of proton-noise decoupling two equal-intensity sharp lines were observed ($\Delta \delta$ = 0.955).

On cooling the sample in CD$_2$Cl$_2$-CS$_2$ the ring proton bands broadened as in the previous cases. At the lowest temperature reached, −110 °C, a very broad complex band envelope comprising at least nine bands was observed. However, band assignments to individual conformers were not possible, thus precluding any subsequent energy-barrier calculations.

Spectral Interpretations.—Saturated five-membered carbocyclic and heterocyclic rings have long been thought to exist in puckered (or half-chair) conformations δ or λ (depending on chirality) or in envelope (or *gauche*) conformations.[10–12] Conformational energy calculations have suggested the half-
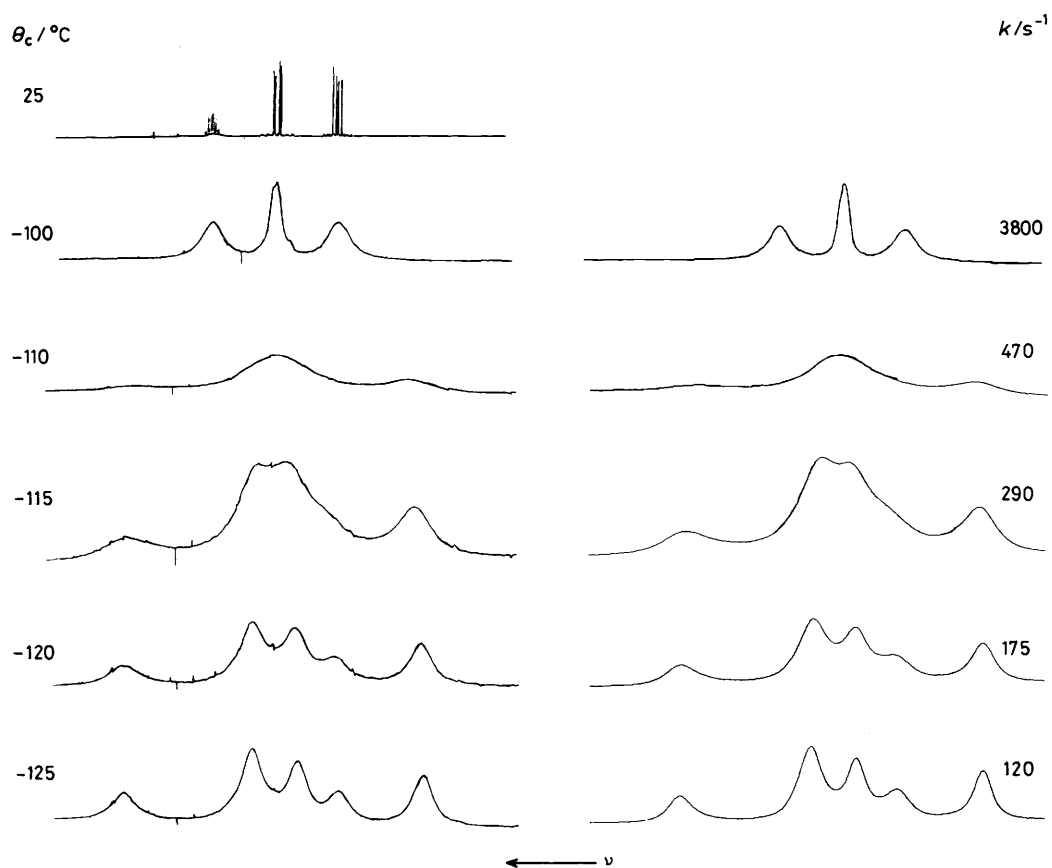

half-chair   envelope

Figure 1. Variable-temperature 400-MHz ^1H spectra of the methylene/methine ring protons of $SnMe_2(SCH_2CHMeS)$, showing the slowing down of the ring-puckering process at low temperatures. Computer-synthesised spectra with ' best-fit ' k values are shown on the right-hand side
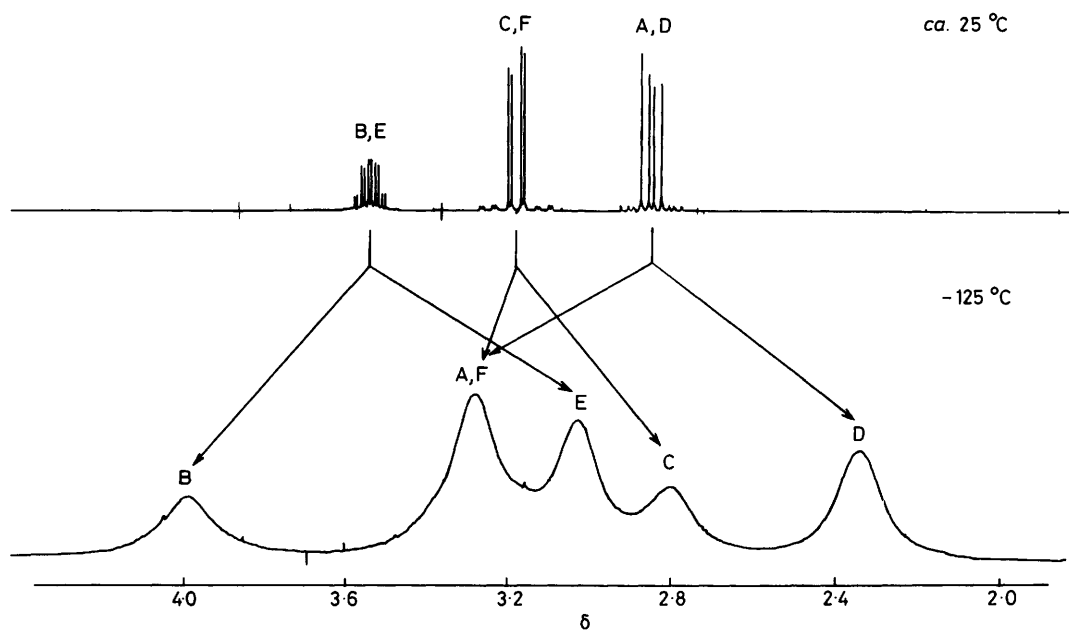

Figure 2. 400-MHz ^1H spectra of $SnMe_2(SCH_2CHMeS)$ showing the relationship between the ambient- and low-temperature spectra. See text for the labelling of the lines
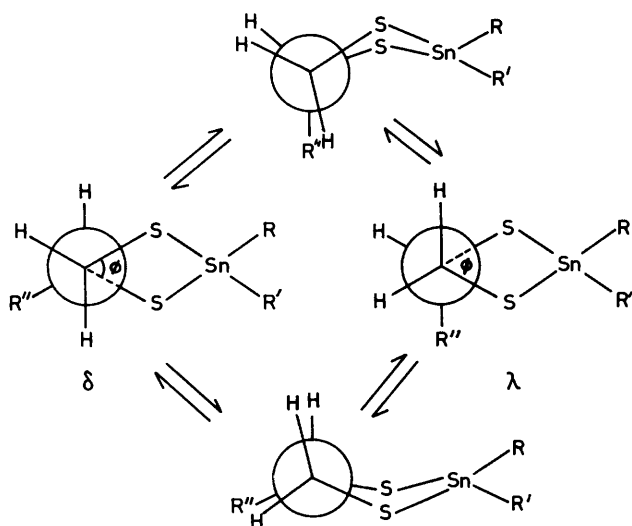
Figure 3. Proposed scheme for the interconversion of the half-chair conformers *via* the envelope intermediates

chair conformations to be somewhat more stable than the envelope structures and this has been confirmed for five-membered diamine chelate rings in both the crystalline state [13] and in solution.[14-16] In the case of rings involving only light atoms, *e.g.* cyclopentane, 1,3-dioxolanes, and 1,3-dithiolanes, the minimum-energy conformations are not as well defined due to numerous almost equi-energy conformers passed through during the ring puckering (pseudorotation or pseudo-libration) process.[17-19] Little definitive data exist for the conformations of the rings although an earlier n.m.r. study [20] suggests that the 1,3-dithiolane ring is clearly more puckered than the 1,3-dioxolane ring. In view of both this result and particularly that of the *X*-ray structure [5] of $SnMe_2(SCH_2CH_2S)$ where the ring clearly adopts a chiral puckered conformation in the solid state, we will assume for the moment that the minimum-energy configurations of the present compounds are closely described by the half-chair conformations δ or λ, rather than the envelope structures favoured by Delmas and Maire,[3] based on u.v. photoelectron and n.m.r. measurements. Furthermore, since the energy barrier to this half-chair–half-chair interconversion is within the n.m.r. time-scale and therefore relatively slow (compared to usual rates of pseudorotation), we will assume that the transition state is the envelope form (C_s symmetry) as was considered to be the case for the diamine chelate rings.[16] A pseudo-rotation or -libration mechanism which avoided passage through this envelope state is likely to be very facile and not detectable by conventional n.m.r. methods.

The previously described low-temperature n.m.r. spectra are therefore attributed to the interconversion of half-chair forms, δ and λ (Figure 3). It should be noted that, when R = R' and R" = H, both half-chair forms δ and λ are degenerate and likewise both envelope forms. When R $\neq$ R' and R" = H, the δ and λ forms are degenerate but the two envelope states are not and thus, in principle, the $\delta \rightleftharpoons \lambda$ interconversion can occur by two different routes. In all other cases, no degeneracies exist and two interconversion routes are possible.

Band-shape fittings were performed on the ring proton regions of the spectra of $SnMe_2(SCH_2CH_2S)$, SnMePh-(SCH_2CH_2S), and $SnMe_2(SCH_2CHMeS)$, where individual low-temperature conformers were clearly detected.

$SnMe_2(SCH_2CH_2S)$. The dynamic spin problem for the

methylene region is of the type AA'BB' $\rightleftharpoons$ B'BA'A, with the protons labelled as shown below. It should be noted that the
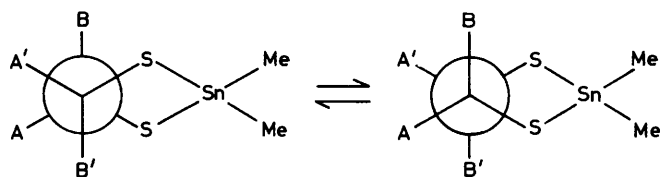
labelling used here differs from that of Sternson *et al.*[20] which is incorrect for 2,2'-dimethyl derivatives. At room temperature the four methylene protons are isochronous as a result of rapid $\delta \rightleftharpoons \lambda$ interconversion, and no J couplings can therefore be measured from the main ^1H signals. However, vicinal coupling-constant data are, in principle, accessible from the ^{13}C satellite spectrum of the methylene signal.[20] However, an attempt to measure such couplings in the present case failed, probably as a result of the limited dynamic range of the n.m.r. computer system used. The band-shape fittings were therefore based on (*i*) the J couplings measured from the ambient-temperature spectrum of $SnMe_2(SCH_2CHMeS)$ and (*ii*) chemical shifts extrapolated from the lowest experimentally measurable values (Table 1). The values chosen are considered to be reliable since satisfactory band fittings could not be achieved with other values. The Arrhenius and activation-energy parameters, listed in Table 3, are based on accurate fittings of four spectra in the range −100 to −125 °C. The uncertainties are standard deviations, σ, those for $\Delta G^{\ddagger}$ being given by $|\sigma(\Delta H^{\ddagger}) - T\sigma(\Delta S^{\ddagger})|$ as discussed by Binsch and Kessler.[21]
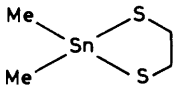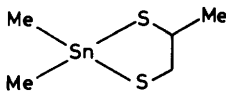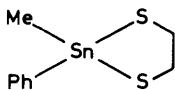
$SnMePh(SCH_2CH_2S)$. Here the dynamic spin problem is strictly of the type ABCD $\rightleftharpoons$ DCBA where the labelling is as shown below. However, at ambient temperatures the
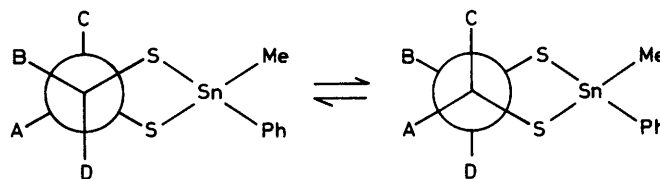

chemical shift difference between the averaged signals $\langle AB \rangle$ and $\langle CD \rangle$ due to the shielding anisotropy of Ph was too small to be detected; nor was it detectable at the lowest temperature due to the residual dynamic broadening of the bands. The spin problem was therefore approximated to the type EF $\rightleftharpoons$ FE, where E $\equiv \langle AB \rangle$ and F $\equiv \langle CD \rangle$, and the fitting problem was of the same type as the previous compound.

$SnMe_2(SCH_2CHMeS)$. The presence of the ring methyl adds substantially to the dynamic spin problem but, at the same time, it provides greater insight into the ring conformational process by virtue of the complex band-shape changes which occur. The two low-temperature conformers were detected in the abundance ratio of 0.42 : 0.58 (Figures 1 and 2). These are respectively assigned to the conformers with axial and equatorial ring methyls, on the basis of the relative magnitudes of non-bonded methyl–methyl interactions. The spin problem is of the type $ABCX_3 \rightleftharpoons DEFY_3$ shown overleaf. The assignments of the labelled protons in this scheme to the ambient- and low-temperature bands in Figure 1 are based on (*i*) the Karplus relationship [9] between vicinal couplings and dihedral angles relating proton pairs and (*ii*) the well founded

Table 3. Arrhenius and activation parameters for the five-membered ring-puckering process of dithiastannolanes

Complex	E_a/kJ mol^{-1}	$\log_{10}A$	$\Delta G^{\ddagger\,a}$/kJ mol^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
	24.4 ± 0.9	11.5 ± 0.3	31.6 ± 0.8	23.1 ± 0.9	-28.6 ± 5.7
	30.9 ± 4.8	12.8 ± 1.6	30.3 ± 4.0	29.6 ± 4.7	-2.5 ± 30.4
	26.4 ± 0.6	11.8 ± 0.2	31.6 ± 0.5	24.9 ± 0.6	-22.3 ± 3.8

^{a} Calculated for $T = 298.15$ K.
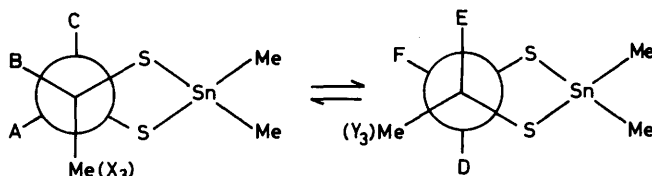
assumption that ring protons in pseudoaxial environments will be more highly shielded than protons in pseudoequatorial environments.[22] This interconversion of two six-spin systems is too large a problem to be handled by the largest version of our general band-shape computer program. Unfortunately, as a result of the various non-zero J coupling constants, the computation cannot be rigorously split into a number of sub-spin problems. We were therefore forced to adopt an approximate method of computation which we nevertheless feel can be totally justified in view of the gross line broadenings produced by the ring conformational process. The splittings of the lines by indirect J couplings are an order of magnitude smaller than effects of chemical shift averagings and can be ignored to a first approximation. Preliminary band fittings were therefore performed on this basis. Subsequent refinements to give the 'best-fit' values (Figure 1) were based on fittings of the dynamic system ABCX $\rightleftharpoons$ DEFY which was the closest approach to the correct formulation that we could achieve. The J values used were taken from the room-temperature spectrum in the absence of any other data. The band-shape fittings were found to be very sensitive to the chemical shift values of the six protons but *not* to the J values. The static parameters used are given in Tables 1 and 2 and the computed band shapes shown alongside the experimental spectra in Figure 1. Although the energy parameters (Table 3) have larger associated errors than usual we have confidence in their reliability. The values quoted are also based on some fittings of the CH$_3$–Sn region which were carried out as a check on the fittings to the methylene region.

SnMePh(SCH$_2$CHMeS). The analyses of the preceding spectra go a long way towards explaining why it was not possible to interpret the low-temperature spectra of this compound. The presence of two structural isomers means that at low temperatures 12 distinct chemically shifted signals for the methylene/methine protons are expected. Nine can be detected

with some certainty in the complex band envelope at -110 °C but cooling by a further 15—20 °C would have been required to have identified all 12 signals. Unfortunately, this did not prove possible on any instrument available to us.

Discussion

The Arrhenius and activation-energy data given in Table 3 are, to our knowledge, the first reported puckering energies of five-membered sulphur-heterocyclic rings measured by d.n.m.r. spectroscopy. In 1,3-dioxolane[17] and 1,3-dithiolane[20] the ring puckering process was much too fast to effect any line-shape changes in the accessible low-temperature range of any n.m.r. spectrometer. In 2-substituted 1,3-dithiolanes the geminal methylene couplings (-11.2 to -11.5 Hz) are appreciably more negative than in the 1,3-dioxolanes (-7.1 to -7.3 Hz). This is attributed to the electronegativity difference between S and O and the greater puckering of the S-heterocyclic rings. In the compounds SnMe$_2$(SCH$_2$CHMeS) and SnMePh(SCH$_2$CHMeS) J_{gem} is -12.45 and -12.38 Hz respectively, which suggests an even greater degree of puckering when a tin atom is also incorporated in the ring. Lambert[23] has demonstrated that the ratio J_{trans}/J_{cis} ($=R$) for $^-$CH$_2$CH$_2^-$ moieties in non-aromatic six-membered rings may be reliably used for predicting molecular ring shape, high values indicating highly puckered rings. Buys[24,25] has used this criterion together with a modified Karplus equation to give the relationship (1) between R and

$$R = 4 \cos^2 \varphi \,(3 - 2 \cos^2 \varphi) \qquad (1)$$

the ring torsional angle φ (Figure 3). This equation gave torsional angles of approximately ±49 and $\pm42°$ for 1,3-dithiolanes and 1,3-dioxolanes respectively, in good agreement with X-ray data. In the compounds SnMe$_2$(SCH$_2$CHMeS) and SnMePh(SCH$_2$CHMeS), $J_{trans} = 7.6$ and 7.7 Hz, and $J_{cis} = 3.0$ and 3.1 Hz respectively, giving $R = 2.5$ in both cases. This relatively high value[20] provides further evidence of a very high degree of puckering in the dithiastannolane ring. Application of equation (1) leads to a value of $\varphi = 60°$, implying that, in the case of the half-chair conformer, the $^-$CH$_2$–CH$_2^-$ moiety is in a fully staggered conformation, or in the case of the envelope conformer the angle by which the SCCS plane

has moved out of the SSnS plane is 60°. The latter structure can, however, now be clearly discounted since (i) the dihedral angles of 0 and 120° relating vicinal protons in this structure are *not* compatible with the magnitudes of the observed vicinal couplings and (ii) the crystal structure of SnMe₂-(SCH₂CH₂S), possessing an $S(1)-C(1)-C(2)-S(2)$ torsional angle of 61.2°, is in almost exact agreement with our calculation of the solution structure. We can therefore conclude that in solution the dithiastannolane five-membered ring adopts a highly puckered half-chair conformation, very similar to that adopted in the solid state. The main difference between solid and solution structures is the absence in the latter of intermolecular S ⋅⋅⋅ Sn contacts and the approximate tetrahedral four-co-ordination of tin.

Interconversion of the half-chair forms of these compounds is relatively slow compared to usual rates of five-membered ring pseudorotations (or pseudolibrations) and can be measured by d.n.m.r. methods. The $\Delta G^{\ddagger}$ values obtained for the process are in the range 30—32 kJ mol⁻¹ and are essentially independent of substituents either on tin or on the five-membered ring. The values are similar but somewhat lower than those calculated for five-membered diamine rings chelated to Cr, Mo, and W.[16] In these systems strain-energy calculations have shown that the barrier to conformational interconversion depends very much on the M-N bond length, such that when this bond is ⩾230 pm the rate process becomes measurable by n.m.r. In our tin(IV) compounds the Sn-S distances are *ca.* 244 pm [5] and the SSnS angles are 89—90°. Such long bonds and acute bond angles can only be accommodated in a five-membered ring with considerable distortion from planarity. Whilst both the half-chair and envelope forms could accommodate such distortions to similar extents,[26] the envelope form is likely to be less stable than the half-chair form as a result of the unfavourable interactions associated with the eclipsing of the -CH₂CH₂- moiety. These tin(IV) compounds therefore adopt a ground-state, highly puckered, half-chair form (of C_2 symmetry when R = R′ and R″ = H).

The present tin(IV) compounds also exhibit interesting fluxional properties at above-ambient temperatures and we will shortly report on these.

The influence of other Group 4 elements (*e.g.* Si) and Group 5 elements (*e.g.* P) in place of Sn on the ring-puckering barriers of these 1,3-dithiolane rings is currently being investigated.

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