The Characterisation of 1,1-Diphenylstannacyclopentane and 1,1,6,6-Tetraphenyl-1,6-distannacyclodecane. An *X*-Ray Diffraction Study of the Distannacyclodecane

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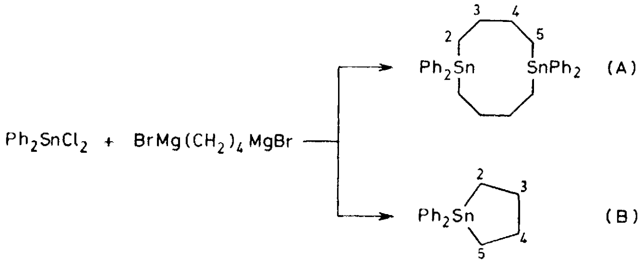
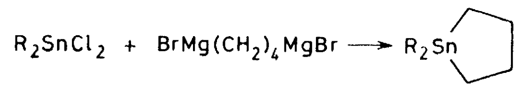
The first oligomeric stannacycloalkane, 1,1,6,6-tetraphenyl-1,6-distannacyclodecane (A) has been isolated, together with the monomer, 1,1-diphenylstannacyclopentane (B), from the reaction between butane-1,4-diyldimagnesium dibromide and diphenyltin dichloride. These compounds have been characterised by molecular weight measurements and by i.r., mass, ^{13}C, and ^{119}Sn n.m.r. spectroscopy. In (A), the ^{13}C n.m.r. signal of C-3 shows two pairs of satellites from coupling to the two tin nuclei, ^{2}J 19.4 and ^{3}J 38.0 Hz. In (B), the ^{13}C signal of C-3 shows one pair of satellites, $^{2/3}J$ 19.6 Hz, which can be regarded as resulting from the algebraic sum of the two-bond and three-bond mediated couplings. The structure of the distannacyclodecane (A) has been determined by single-crystal *X*-ray diffraction. It has a boat-chair-boat structure, similar to that of cyclodecane itself, with the Ph_2Sn groups replacing those methylene groups which are not subject to steric hindrance. The principal features of the structure of the stannacyclopentane (B) are apparent from a preliminary *X*-ray study. It has a twisted conformation of C_2 symmetry, with a twist angle of *ca.* 15° and an endocyclic angle at tin of 95°.

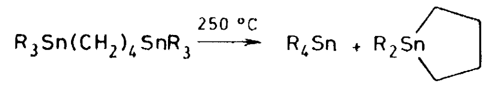


If dialkyltin dichlorides are treated with butane-1,4-diyldimagnesium dibromide, the corresponding 1,1-dialkylstannacyclopentanes (I) can be isolated in moderate yield [equation (1), $R_2 = Bu_2$,[1,2] $(Bu^tCH_2)_2$,[1] Me_2,[2-4] $Me(Bu^tCH_2)$,[3] Et_2[2]]. The same compounds can also be prepared in better yield by the thermal disproportionation of the corresponding 1,4-bis(trialkylstannyl)butanes [equation (2), R = Me,Et].[5]



(1)

(I)

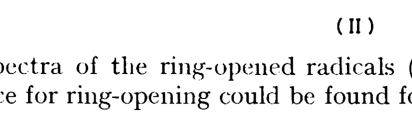


(2)

There seems no doubt that, when R is an alkyl group, the products which have been isolated from reactions (1) and (2) are authentic stannacyclopentanes. Typical examples of compound (I) show the expected molecular weights (presumably measured in solution) [$R_2 = Bu_2$: found 284, calculated 289. $R_2 = (Bu^tCH_2)_2$: found 314, calculated 317],[1] and this is consistent with the mass spectrum ($R_2 = Me_2$) which shows the molecular ion $[Me_2Sn(CH_2)_4]^{+\cdot}$ as the largest fragment.[3]

Molecular models show that the formation of an SnC_4 ring must involve substantial angle strain, and this strain has been invoked to explain the enhanced heterolytic [1,5] and homolytic [2] reactivity of the ring, and the fact that the ^{119}Sn nucleus in 1,1-dimethylstannacyclopentane shows an n.m.r. chemical shift *ca.* 50 p.p.m. downfield from that in acyclic tetra-alkyltins.[4] It may also contribute to the high refractive index.

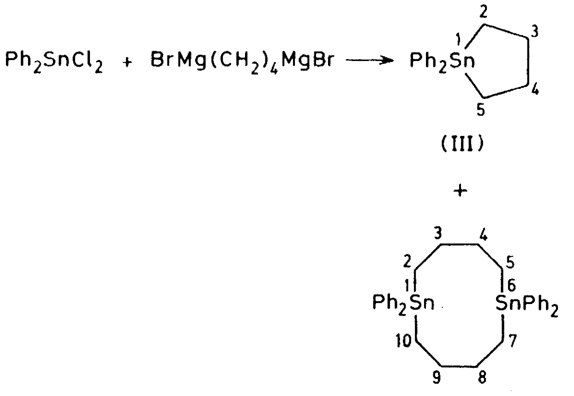
Treatment of diphenyltin dichloride with butane-1,4-diyldimagnesium dibromide [equation (1), R = Ph] has been reported to give a low melting solid [3,6] which has been assumed also to have the stannacyclopentane structure (I; R = Ph) although direct evidence is lacking. Our doubts about the generality of this structure were raised when we found that, whereas the dialkylstannacyclopentanes reacted readily with a variety of oxygen-centred radicals [equation (3)] to show e.s.r. spectra of the ring-opened radicals (II); no such evidence for ring-opening could be found for a specimen of the diphenyl compound prepared by the above method.[2]



(3)

(II)

We report here the isolation of both 1,1-diphenylstannacyclopentane (III) and 1,1,6,6-tetraphenyl-1,6-distannacyclodecane (IV) from the Grignard reaction (4). These compounds have been characterised by i.r., ^{13}C n.m.r., ^{119}Sn n.m.r., and mass spectrometry, and (by e.s.r. spectrometry) by their reactivity towards t-butoxyl radicals, and the structure of the distannacyclodecane (IV) has been determined by single-crystal *X*-ray diffraction.



(III)

(4)

(IV)

EXPERIMENTAL

Preparation of 1,1-*Diphenylstannacyclopentane and* 1,1,6,6-*Tetraphenyl*-1,6-*distannacyclodecane*.—Following Zimmer's general method,[1] a solution of diphenyltin dichloride (17 g) in diethyl ether (300 cm^3) was added to the di-Grignard reagent derived from 1,4-dibromobutane (1 mol. equiv.) in ether (120 cm^3) at room temperature. The mixture was heated under reflux for 2 h, and hydrolysed with 1M-hydrochloric acid. Ether was removed from the organic layer to leave an oil which was distilled to give 1,1-diphenylstannacyclopentane (*ca.* 6 g), b.p. 140—142 °C at 0.5 mmHg, which solidified on standing to give needles, m.p. 33 °C (Found: C, 59.1; H, 6.0. Calc. for $C_{16}H_{18}Sn$: C, 58.4; H, 5.5%).

A similar reaction was carried out on the same scale using tetrahydrofuran as solvent (total volume 100 cm^3). The mixture was heated under reflux for 3 h, then hydrolysed with aqueous ammonium chloride, and tetrahydrofuran was removed from the organic layer at room temperature leaving an oil. This was dissolved in pentane and kept in the refrigerator overnight, when 1,1,6,6-*tetraphenyl*-1,6-*distannacyclodecane* separated as waxy rhombs (*ca.* 1 g), m.p. 96—98°, b.p. 225 °C (bath) at 0.001 mmHg (Found: C, 58.6; H, 5.5. $C_{32}H_{36}Sn_2$ requires C, 58.4; H, 5.5%).

Physical Methods.—Molecular weights were measured at 37 °C in benzene solution, using a Mecrolab 302A vapour pressure osmometer, calibrated against benzil. I.r. spectra were recorded on the supercooled melts on a Unicam SP 1000 spectrometer. ^1H N.m.r. spectra were recorded at 60 MHz on a JEOL C60-H spectometer, and ^{13}C spectra at 15 MHz on a JEOL FX-60 Fourier transform instrument. The ^{119}Sn data were obtained by the ^1H-{^{119}Sn} double resonance technique using a modified JEOL C60-H instrument.[4] E.s.r. spectra were recorded with a Varian E4 spectrometer, fitted for photolysis within the cavity.[2] Mass spectra were determined on an AEI MS9 instrument at 70 eV and a source temperature of 70 °C.

X-Ray Diffraction.—The distannacyclodecane (IV) crystallises from pentane with an acicular habit, elongated parallel to the *y*-axis, and bounded mainly by the forms {101} and {$\bar{1}$01}. Oscillation and Weissenberg *X*-ray photographs showed that the crystals were monoclinic, with space group $P2_1/c$. Accurate unit cell dimensions were obtained by a weighted ($\omega = \tan\theta$) least-squares fit to the θ values of 17 reflexions for which both $\theta > 45°$ and the $\alpha_1\alpha_2$ peaks were resolved.

Intensity data were collected on a Siemens four-circle diffractometer (AED). Within the range $0.0565 < (\lambda^{-1}\sin\theta) < 0.563$, 2 166 symmetry-independent reflexion intensities were measured; 317 of them, for which $I < 2.58\,\sigma(I)$, were classed as ' unobserved ', and omitted from analysis. The intensities were corrected for Lorentz and polarization effects, but not for absorption. The reference reflexion monitor varied in intensity by no more than ±3% during the data collection period, from which evidence, as well as from visual inspection, the crystal was deemed to have undergone no decomposition.

The structure was solved by the heavy-atom technique: the Sn–Sn Patterson peaks were of positions and weights demanded by the space-group symmetry. The positions of the tin atoms were refined isotropically to *R* 20%, and the non-hydrogen atoms were located on a difference-Fourier synthesis. Refinement was carried out isotropically to *R* 8%: then the hydrogen atom positions were determined from standard molecular geometry, and refined isotropically, while the other atoms were refined anisotropically. A dispersion correction was applied to the tin atoms, and weights, given by the equation $w = A + |F_o|^2 + B|F_o|^2 + C|F_o|^3$, and $A = 61$, $B = -5.2 \times 10^{-3}$, and $C = 1.9 \times 10^{-3}$ were applied.

The refinement converged at *R* 4.4%. The final difference-Fourier map showed peaks up to 1 e Å^{-3} in the neighbourhood of the tin atoms, but less than 0.2 e Å^{-3} elsewhere. The weighting scheme was confirmed by adequate constancy of $\omega\Delta^2$, $\Delta = |F_o| - |F_c|$, over eight ranges of $|F_o|$.

Crystals of 1,1-diphenylstannacyclopentane (III) were obtained, with a tabular habit, by recrystallization from pentane. They exhibited the forms, in decreasing order of development, {010}, {101}, {100}, and {001} under orthorhombic hemimorphic symmetry. *X*-Ray diffraction photographs showed that the crystals belonged to space group *Aba*2 or *Abam*. From consideration of both the possible molecular symmetry and the crystal density, *Aba*2 was chosen. Accurate unit-cell dimensions were obtained by a weighted least-squares fit ($\omega = \tan\theta$) to the θ values of 20 high-order reflexions measured on a Siemens four-circle diffractometer: $a = 10.175(2)$, $b = 16.379(3)$, $c = 8.956(2)$ Å. Four molecules ($C_{16}H_{18}Sn_2$) per unit cell correspond to a density of 1.462 g cm^{-3}.

Intensity data were collected on the Siemens diffractometer, with Cu-K_α radiation (λ 1.5418 Å) to $\theta_{max.} \leqslant 65°$. A total of 679 reflexions was obtained, of which 190 were classified as unobserved at the 3σ level and omitted from the analysis. The intensities were corrected for Lorentz, polarization and absorption (μ 137 cm^{-1}) effects.

The choice of the non-centrosymmetric space group was supported by the results of an $N(z)$ test, and the presence of four molecules in the unit cell indicated that the molecules lie on two-fold axes passing through the tin atom and the symmetrically placed C–C bond of the stannacyclopentane ring.

The structure was solved by the heavy-atom technique. The Patterson map confirmed the location of the molecules on the two-fold axes, and electron-density maps phased on tin revealed the remaining atoms of the molecule. The structure was refined by anisotropic least-squares calculation to an *R* factor of 16%. So far, a better refinement has not been achieved because, we think, the crystal at room temperature is close to its m.p. The molecule adopts a twist (*ca.* 15°) conformation (see Discussion). The average C–C bond lengths and average angles at carbon in this ring are 1.5 Å and 115°, respectively. The unique Sn–C bond lengths are 2.1 Å and the angles at tin are 95 (endocyclic) and 120° (exocyclic), indicating a considerable degree of strain in the five-membered ring. The phenyl rings are planar and their C–C bond lengths and angles at carbon average to 1.4 Å and 120°, respectively. There are no abnormal van der Waals contact distances in the crystal structure.

RESULTS

Molecular weights and n.m.r. data are listed in Table 1. The i.r. spectra are illustrated in Figure 1 and the ^{13}C n.m.r. spectra in Figure 2. The monoisotopic mass spectra, based on ^{120}Sn, are tabulated in Table 2.

The crystallographic results are listed in Tables 3 and 4. The atomic co-ordinates study are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for our preliminary communication (ref. 7).

DISCUSSION

The Properties of the Monomer and Dimer.—From the crude product of reaction (4), the monomer (III) can be isolated by distillation, and the dimer (IV) by crystallisation.

The measurements of molecular weights in solution confirm that the two compounds are related as monomer and dimer, and similar measurements on the dialkylstanna-cyclopentanes, -cyclohexanes, and -cycloheptanes which we described previously[8] confirmed that they were the monomers which they had been assumed to be.

TABLE 1

M.p., b.p., molecular weight (m.w.), and n.m.r. parameters of 1,1-diphenylstannacyclopentane (III) and 1,1,6,6-tetraphenyl-1,6-distannacyclodecane (IV)

		(III)	(IV)
M.p.		33 °C	96—98 °C
B.p.		140—142 °C at 0.5 mmHg	225 °C (bath) at 0.001 mmHg
M.w.	Found	303, 315	666, 681
	Calc.	329	658
N.m.r.	δ^{119}Sn/p.p.m.[a]	0 ± 2	-74 ± 2
	δ^{13}C$_\alpha$/p.p.m.[b]	10.7	10.5
	δ^{13}C$_\beta$/p.p.m.	32.3	29.8
	$^1J(^{119}\text{Sn}-^{13}\text{C})$/Hz[d]	-349	$+368$
	$^2J(^{119}\text{Sn}-^{13}\text{C})$/Hz[d]	-19.6[c]	-19.4
	$^3J(^{119}\text{Sn}-^{13}\text{C})$/Hz[d]		38
	$^4J(^{119}\text{Sn}-^{13}\text{C})$/Hz[d]		<7

[a] With respect to tetramethyltin, in dichloromethane as solvent. Downfield shifts are taken as positive. [b] With respect to tetramethylsilane, in dichloromethane as solvent. [c] $^{2/3}J$. [d] Note that $\gamma(^{119}\text{Sn})$ is negative.

The dimer (IV) could be distilled at 225 °C (bath) and 0.001 mmHg, and recovered with the mass spectrum unchanged. The monomer and dimer, and probably higher oligomers, are thus apparently the primary products of the reaction of butane-1,4-diyldimagnesium dibromide with diorganotin dichlorides, and are not readily interconvertible.

It should be noted that we have recently observed that a pure sample[4] of the dimethyl analogue $\text{Me}_2\text{Sn(CH}_2)_4$ sealed under nitrogen and kept for several years at 20 ± 5 °C in the absence of light underwent extensive oligomerisation to give the dimer together with smaller but significant amounts of what are probably the trimer $[\text{Me}_2\text{Sn(CH}_2)_4]_3$ and tetramer $[\text{Me}_2\text{Sn(CH}_2)_4]_4$. In the general case however, the diphenyltin derivatives are probably special only in that the dimer (IV) is a solid of limited solubility which separates readily from nonpolar solvents.

The i.r. spectra of the monomer (III) and dimer (IV) (Figure 1) show significant differences in the positions and intensities of absorptions in the region 850—1 350 cm^{-1}, and, in particular, the dimer is characterised by peaks at 1 270, 1 310, and 1 350 cm^{-1} which are absent or much weaker in the monomer. Dr. J.-C. Pommier has provided us with a copy of the i.r. spectrum of the compound which was prepared by M. Bourhis in 1965,[6] and this corresponds unambiguously with our spectrum of the monomer (Figure 1a).

The ^{1}H n.m.r. spectra at the lower magnetic fields available to us are poor criteria of identity, but the ^{119}Sn and ^{13}C spectra can readily distinguish between the two compounds.

The incorporation of tin into a five-membered ring has the effect of shifting the ^{119}Sn resonance to low field,[4,9] probably because of the reduction of interbond angles; for example $\delta(^{119}\text{Sn})$ for dimethylstannacyclopentane is 47 p.p.m. downfield from diethyldimethyltin. This effect is apparent in a comparison of the stannacyclopentane (III) and the distannacyclodecane (IV). Whereas (IV) shows a ^{119}Sn chemical shift close to that of the acyclic analogue, diethyldiphenyltin (—66 p.p.m.), the ^{119}Sn resonance in (III) is shifted downfield by 74 p.p.m.

The values for $\delta(^{13}\text{C})$ and for $^1J(^{119}\text{Sn}-^{13}\text{C})$ (Table 1) are similar in both compounds, but the longer range $^{119}\text{Sn}-^{13}\text{C}$ couplings display important differences. In this connection it should be pointed out that most of the 'strain' is taken up at the more deformable tin atom, as confirmed by the *X*-ray diffraction studies.

In the dimer (IV), the equivalent ^{13}C(-3), (-4), (-7), and (-8) nuclei are located in the β-position with respect to one tin atom, and in the γ-position with respect to the other, and they display two separate sets of ^{119}Sn satellites with $|J(^{119}\text{Sn}-^{13}\text{C})|$ 19 and 38 Hz as shown in Figure 2. Related work on cyclic organotin compounds suggest that the assignments[10] and signs[11,12] are $^2J(^{119}\text{Sn}-^{13}\text{C}) + 19$ and $^3J(^{119}\text{Sn}-^{13}\text{C}) - 38$ Hz, as shown in (V), and we have confirmed by selective double resonance that the two-bond mediated coupling in

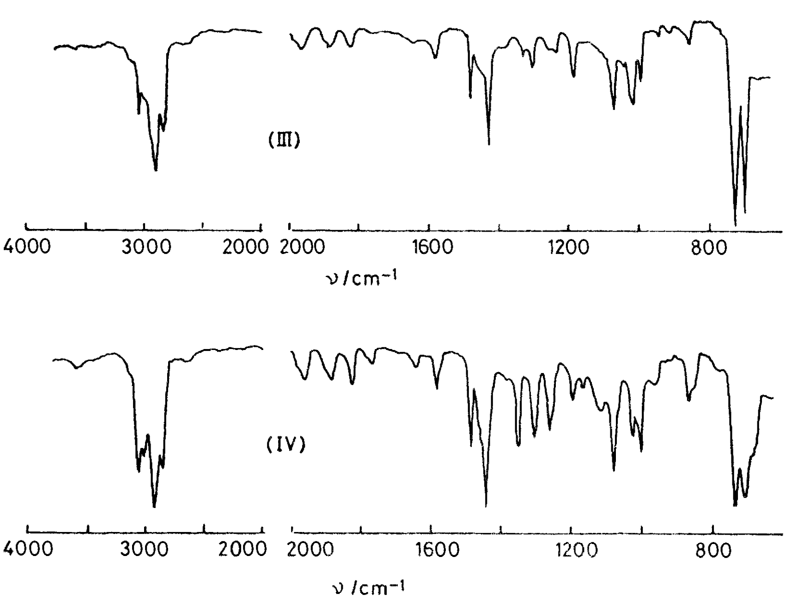


FIGURE 1 I.r. spectra of super-cooled melts of 1,1-diphenylstannacyclopentane (III) and 1,1,6,6-tetraphenyl-1, 6-distannacyclodecane (IV)

1,1-diphenylstannacyclohexane * has a positive sign, ${}^2J({}^{119}\text{Sn}-{}^{13}\text{C})$ + 29 Hz.

In the monomer (III), the ^{13}C(-3) and (-4) nuclei are situated in both the β- and the γ-position with relation to the one tin nucleus, and there are available a two-bond and a three-bond path for the electron-mediated coupling as shown in (VI). If ${}^{2/3}J({}^{119}\text{Sn}-{}^{13}\text{C}) = {}^2J({}^{119}\text{Sn}-{}^{13}\text{C}) + {}^3J({}^{119}\text{Sn}-{}^{13}\text{C})$, the observed coupling should be +19 − 38 = *ca.* −19 Hz, and indeed the spectrum (Figure 2) shows a single pair of satellites with ${}^{2/3}J$ − 19.6 Hz, the sign of the coupling being established by selective double resonance.

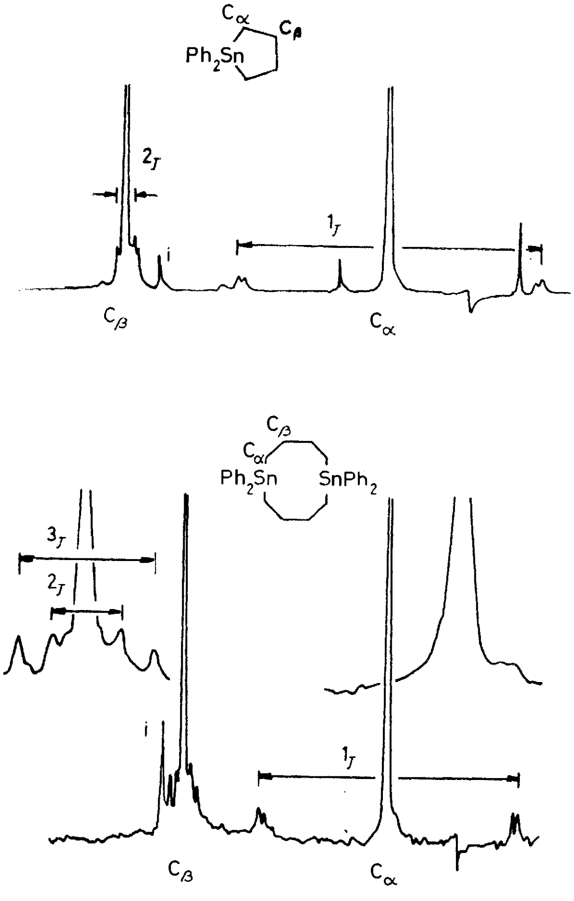
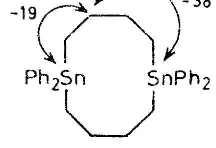
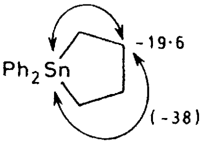


FIGURE 2 ^{13}C N.m.r. spectra of 1,1-diphenylstannacyclopentane and 1,1,6,6-tetraphenyl-1,6-distannacyclodecane. The peaks marked i are due to impurities



(V)



(VI)

The quantitative agreement is probably fortuitous because we have ignored the dependence of ${}^2J$ and ${}^3J$ on factors such as the hybridisation of the atoms involved and the stereochemical relationship between the nuclei, but the additivity of the two paths for coupling does account qualitatively for the value which is observed. Certainly however, a value of −19.6 Hz is abnormal for *either* ${}^2J({}^{119}\text{Sn}-{}^{13}\text{C})$ *or* ${}^3J({}^{119}\text{Sn}-{}^{13}\text{C})$ taken alone.

The mass spectrum of 1,1-diphenylstannacyclopentane (III) at 70 eV and 70 °C showed as principal fragments the ions $\text{Ph}_2\text{SnC}_4\text{H}_8{}^{+\cdot}$, $\text{Ph}_2\text{Sn}^{+\cdot}$, and $\text{Sn}^{+\cdot}$ (see Table 2). These results are similar to those reported by Gielen and Topart,[3] and confirm that their compound (m.p. 39 °C), which was prepared by reaction (4), was indeed the authentic stannacyclopentane; differences in intensities between their results and ours may be due largely

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* Molecular weight; Found: *M*, 350.6, 347.0, 341.3. Calc. for $\text{C}_{17}\text{H}_{20}\text{Sn}$: *M*, 343.1. It should be noted that ^{119}Sn has a negative magnetogyric ratio, and therefore the reduced coupling constant *K* will be of opposite sign to *J*.

TABLE 2

Principal fragments observed in the mass spectra of 1,1-diphenylstannacyclopentane (III) and 1,1,6,6-tetraphenyl-1,6-distannacyclodecane (IV)

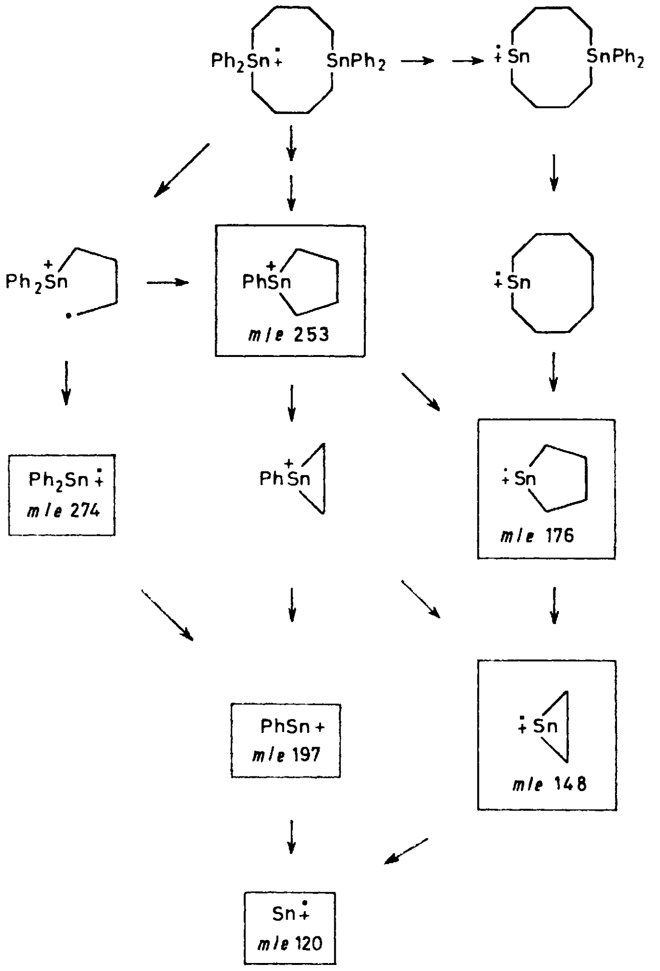
m/e	(III) Intensity (%) [a]	(IV) Intensity (%) [a]	Probable fragment
120	40.5	22.4	Sn
145			C_2HSn
148	1.1	5.9	C_2H_4Sn
169	1.1		
171	1.6		
176		4.7	C_4H_8Sn
197	33.9	29.1	PhSn
225		1.8	$PhSnC_2H_4$
232		3.9	$C_8H_{16}Sn$
252	0.6		
253	0.6	19.0	$PhSnC_4H_8$
274	9.2	3.9	Ph_2Sn
302	0.6		
310		3.6	$PhSnC_8H_{17}$
330	5.4	2.8	$Ph_2SnC_4H_8$
352		2.2	$Sn_2C_8H_{16}$
356		0.6	

[a] Percentage of total intensity of listed fragments. Some tin-free hydrocarbon ions could also be detected, but their intensities were much less than those which are listed.

to the higher temperatures of their source (250 rather than 70 °C). Gielen and Topart proposed a reasonable route by which the fragmentation may proceed.[3]

The mass spectrum of 1,1,6,6-tetraphenyl-1,6-distannacyclodecane is substantially different (see Table 2). The ions $Ph_2SnC_4H_8^{+\cdot}$, $Ph_2Sn^{+\cdot}$, $PhSn^+$, and $Sn^{+\cdot}$ are still prominent, but now the ion $PhSnC_4H_8^+$ is a major component. Fragments with *m/e* 352 ($^{+\cdot}Sn_2C_8H_{16}$) and 232 ($^{+\cdot}SnC_8H_{16}$) confirm the presence of two tin atoms and eight methylene groups in the molecule, and significant fragments are also observed at *m/e* 176 ($^{+\cdot}SnC_4H_8$) and 148 ($^{+\cdot}SnC_2H_4$). A reasonable route for the fragmentation is shown in the Scheme.

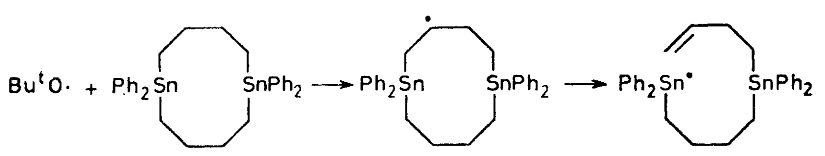
The reactivity of the compounds towards t-butoxyl radicals by reaction (3; $X^\cdot = Bu^tO\cdot$), as shown by e.s.r. spectroscopy, also distinguishes clearly between (III) and (IV). Whereas photolysis of di-t-butyl peroxide in the presence of the dimer (IV) did not show the spectrum of any recognisable radical, the same reaction with the monomer (III) showed a strong spectrum of the ring-opened radical (IX) [$a(2H_\alpha)$ 22.0, $a(2H_\beta)$ 27.8, $a(2H_\gamma)$ 0.9 G at −80 °C] similar to that which has been reported for other stannacyclopentanes.[2]



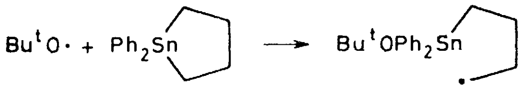
SCHEME Possible fragmentation pattern for 1,1,6,6-tetraphenyl-1,6-distannacyclodecane. The principal fragments which are observed are boxed

With (IV), hydrogen may be abstracted from the β-methylene group, to give the radical (VII) which undergoes β-scission to give the tin-centred radical (VIII) with a broad spectrum which is difficult to detect.[2,8] With (III), angle strain confers an unusually high reactivity at the tin centre.[2]

The Structure of 1,1,6,6-*Tetraphenyl*-1,6-*distannacyclodecane*.—The structure of the distannacyclodecane (IV) can best be discussed in terms of its relation with cyclodecane itself. Large flexible even-numbered rings are most stable in the conformations which can be traced as

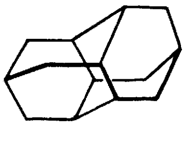


(IV) (VII) (VIII) (5)

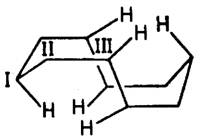


(III) (IX) (6)

fragments of the diamond lattice.[13] The C_{10} ring in the diamond lattice has a boat-chair-boat conformation as shown in (X); *X*-ray diffraction studies confirm that this structure persists in various cyclodecane derivatives in the solid state,[14] and electron diffraction measurements show that this is the preferred conformation in cyclodecane itself as shown in (XI).[15]



(X)



(XI)

The structure (XI) contains three non-equivalent types of methylene group, labelled I—III. On positions I and III, the hydrogen atoms approach within the van der Waals distance above the ' boats ', and provide most of the strain in the molecule.

If a pair of opposed methylene groups are to be replaced by sterically more demanding Ph_2Sn groups, this would be expected to occur at positions of type II, and this indeed is the structure which is established by *X*-ray diffraction, as shown in Figure 3.

The two monomeric units are related by a centre of symmetry.

The phenyl rings are planar within experimental error (Table 4), and assume a favourable orientation with the plane normals forming an angle of *ca.* 115°. Within the rings, the average C–C bond length and C–C–C angle are 1.39 Å and 120°, respectively. The bond angles at tin are tetrahedral, averaging 109° (Table 3).

The Sn–C bond lengths average 2.15 Å, and are not significantly different whether bonded to the phenyl rings or to the carbon atoms within the distannacyclodecane ring. The presence of these long bonds within the ring relieves some of the strain which is present in cyclodecane. The transannular separation of the hydrogen atoms of the methylene groups which in cyclodecane itself is H(I)—H(III) 1.97, H(III)—H(III′) 1.84 Å, is increased to H(I)—H(III) 2.23, H(I)—H(III′) 2.82, (HIII)—H(III′) 2.36 Å, compared with a van der Waals contact distance of 2.4 Å. The average C–C–C angle within the ring at 114° is closer to the tetrahedral angle

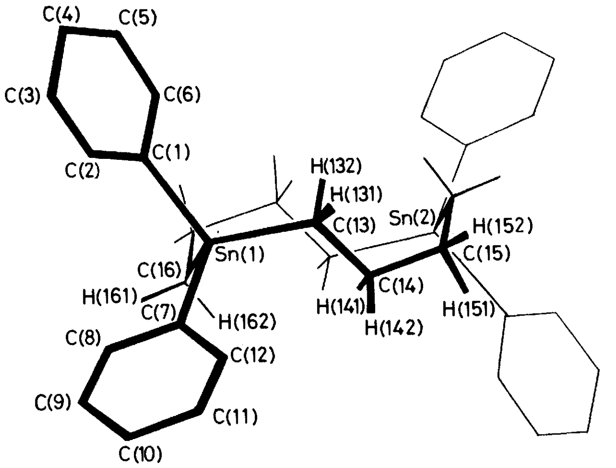


FIGURE 3 Structure of 1,1,6,6-tetraphenyl-1,6-distannacyclodecane

TABLE 3

Bond lengths (Å) and bond angles (°) in 1,1,6,6-tetraphenyl-1,6-distannacyclodecane

Sn(1)–C(1)	2.150(9)	C(13)–H(132)	0.95(5)
Sn(1)–C(7)	2.131(6)	C(14)–H(141)	1.10(7)
Sn(1)–C(13)	2.155(7)	C(14)–H(142)	0.95(6)
Sn(1)–C(16)	2.167(8)	C(15)–H(151)	1.06(9)
C(1)–C(2)	1.38(1)	C(15)–H(152)	1.00(6)
C(2)–C(3)	1.39(2)	C(16)–H(161)	1.01(7)
C(3)–C(4)	1.37(1)	C(16)–H(162)	0.93(10)
C(4)–C(5)	1.37(2)		
C(5)–C(6)	1.39(2)	C(1)–Sn(1)–C(7)	108.2(3)
C(6)–C(1)	1.39(1)	C(1)–Sn(1)–C(13)	107.5(3)
C(7)–C(8)	1.39(1)	C(1)–Sn(1)–C(16)	110.1(3)
C(8)–C(9)	1.39(1)	C(7)–Sn(1)–C(13)	111.0(3)
C(9)–C(10)	1.39(2)	C(7)–Sn(1)–C(16)	106.6(3)
C(10)–C(11)	1.35(2)	C(13)–Sn(1)–C(16)	113.3(3)
C(11)–C(12)	1.41(1)	C(2)–C(1)–C(6)	117.6(9)
C(12)–C(7)	1.40(1)	C(3)–C(2)–C(1)	120.8(7)
C(13)–C(14)	1.53(1)	C(4)–C(3)–C(2)	120.5(10)
C(15)–C(16)	1.52(1)	C(5)–C(4)–C(3)	119.8(12)
C(15)–C(14) [a]	1.54(1)	C(6)–C(5)–C(4)	119.9(8)
		C(1)–C(6)–C(5)	121.4(9)
C(2)–H(2)	0.95(7)	C(8)–C(7)–C(12)	117.9(6)
C(3)–H(3)	1.13(10)	C(9)–C(8)–C(7)	121.3(8)
C(4)–H(4)	1.12(12)	C(10)–C(9)–C(8)	119.5(8)
C(5)–H(5)	1.07(7)	C(11)–C(10)–C(9)	119.8(8)
C(6)–H(6)	1.03(9)	C(12)–C(11)–C(10)	121.5(10)
C(8)–H(8)	1.04(8)	C(7)–C(12)–C(11)	120.0(8)
C(9)–H(9)	1.11(7)	Sn(1)–C(13)–C(14)	114.8(4)
C(10)–H(10)	0.99(7)	Sn(1)–C(16)–C(15)	117.1(5)
C(11)–H(11)	0.88(8)	C(13)–C(14)–C(15) [a]	112.7(6)
C(12)–H(12)	1.09(6)	C(16)–C(15)–C(14) [a]	113.0(7)
C(13)–H(131)	0.89(6)		

[a] Symmetry operation $\bar{x}, \bar{y}, \bar{z}$.

TABLE 4

Mean planes, with deviations of atoms from the planes. Atoms in bold face were included in the calculation of the plane; *X*—*Z* are cartesian Ångstrom coordinates. The e.s.d.s of the deviations are *ca.* 0.006

Plane 1

$$0.4566X - 0.7344Y + 0.5022Z = 0.5699$$

	Δ/Å		Δ/Å
C(1)	0.005	Sn(1)	−0.107
C(2)	−0.013	H(2)	0.062
C(3)	0.008	H(3)	0.167
C(4)	0.005	H(4)	0.021
C(5)	−0.013	H(5)	−0.069
C(6)	0.009	H(6)	0.063

Plane 2

$$-0.6536X + 0.5388Y + 0.5315Z = 1.7671$$

	Δ/Å		Δ/Å
C(7)	−0.008	Sn1	−0.097
C(8)	0.006	H8	0.028
C(9)	−0.001	H9	−0.032
C(10)	−0.001	H10	0.044
C(11)	−0.002	H11	0.108
C(12)	0.007	H12	0.058

Angles between normals of planes 1 and 2, 115.3 °

Plane 3

$$0.9561X + 0.0666Y - 0.2854Z = 0.0000$$

	Δ/Å		Δ/Å
Sn(1)	−0.19	**Sn**(1′)	0.19
C(13)	−0.50	**C**(13′)	0.50
C(14)	0.68	**C**(14′)	−0.68
C(15′)	0.27	**C**(15)	−0.27
C(16′)	−0.64	**C**(16)	0.64

Table 5

Structures of sila- and germa-cyclopentanes from microwave spectroscopy, and of 1,1-diphenylstannacyclopentane from X-ray diffraction

(XII) Bond length(Å)			Bond angles (°)				
M	R	C–M	R–M–R	C–M–C	M–C–C	C–C–C	τ
Si	H	1.87 [a]	108.8	96.7	105.1	113.7	21 [16]
Ge	H	1.95 [a]	111	98	106	115	18 [17]
Sn	Ph	2.1	120	95	115	115	15

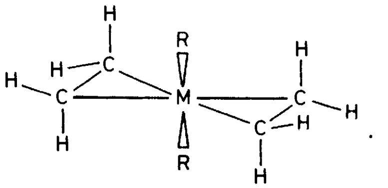
[a] Assumed values.

than it is in cyclodecane (116.5°), and the C–Sn–C angle is 113.3° compared with 116.9° at C(II) in the parent.

The molecules pack with the ' best ' planes of the ten-membered rings approximately normal to the y-axis. There are no abnormal intermolecular contacts, and the molecules are linked only by van der Waals forces.

This structure contains four types of carbon atom in the ring, but, as described above, the ^{13}C n.m.r. spectrum of the solution at room temperature shows only two signals for their atoms. Similarly, cyclodecane in solution shows only one ^{13}C n.m.r. signal. Apparently, in solution, rapid interconversion occurs between the various possible isomers.

The Structure of 1,1-*Diphenylstannacyclopentane.*—We have not yet been able to refine the interpretation of the X-ray diffraction data for 1,1-diphenylstannacyclopentane beyond an R value of 16%, but the principal features of the structure are apparent. The results are presented in Table 5, alongside those from microwave studies on sila-[16] and germa-cyclopentane.[17]



(XII)

All three molecules exist in a twisted conformation of C_2 symmetry as shown in (XII). The tin compound, with the longest C–M bonds, has the smallest twist angle, τ, and, at the metal M, the smallest endocyclic angle (95°) and the largest exocyclic angle (120°) representing the largest deviations from tetrahedrality. The severe angle strain which this represents is constant with the abnormal chemical and physical properties which are associated with the stannacyclopentanes.

The monomer was prepared and the n.m.r. measurements were carried out at Sir John Cass College. The dimer was isolated and the other physical measurements were made at University College. The crystallographic study was carried out at the University of Surrey. We are grateful for helpful correspondence with Dr. J.-C. Pommier and Professor M. Gielen, and we acknowledge support from the S.R.C. and from the International Tin Research Council.

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