Formation and *X*-Ray Crystal Structure of 1,1,6,6-Tetraphenyl-1,6-distannacyclodecane

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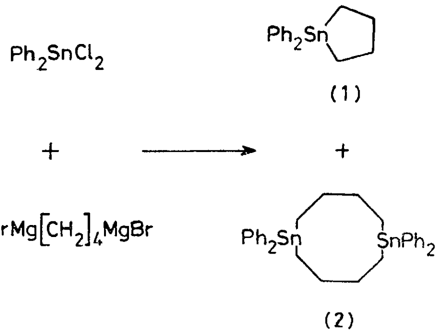
Summary The ^{119}Sn and ^{13}C n.m.r. spectra of 1,1-diphenylstannacyclopentane and 1,1,6,6-tetraphenyl-1,6-distannacyclodecane have been rationalised, and the structure of the latter compound has been shown by single-crystal *X*-ray diffraction to be of the 'boat-chair-boat' type, similar to that of cyclodecane.

The reaction of butane 1,4-dimagnesium bromide with diorganotin dihalides gives the corresponding 1,1-diorganostannacyclopentanes in low yield,[1] together with polymeric material which hitherto has not been identified.[2,3] From the reaction of diphenyltin dichloride we have now isolated and characterised both 1,1-diphenylstannacyclopentane (**1**) and 1,1,6,6-tetraphenyl-1,6-distannacyclodecane (**2**), and have determined the structure of (**2**) by single crystal *X*-ray diffraction. The reaction was carried out by Zimmer's method.[4] Distillation of the product yielded the stannacyclopentane (**1**), b.p. 140 °C at 0·5 mmHg, m.p. 33 °C (lit. m.p. 34,[5] 39 °C[6]), or, on cooling in pentane, gave the distannacyclodecane (**2**) m.p. 96—98 °C, which distilled unchanged, b.p. 225 °C (bath) at 0·01 mmHg. The monomer (**1**) and the dimer (**2**) (and probably higher oligomers) therefore appear to be the products of kinetic rather than thermodynamic control.



Both compounds were characterised by elemental analysis, molecular weight (by vapour pressure osmometry), i.r., n.m.r., Mössbauer, and mass spectra. The ^{119}Sn and ^{13}C n.m.r. spectra are particularly informative.

^{119}Sn N.m.r. spectra were determined by ^{1}H-$\{^{119}$Sn$\}$ double resonance; chemical shifts are reported relative to $Me_4{}^{119}Sn$, downfield shifts being given a positive sign. We have shown previously that the 1,1-dialkylstannacyclopentanes show a downfield shift of *ca.* 50 p.p.m. compared with the corresponding acyclic compounds, probably as a result of angle strain.[7] In accord with this, the stannacyclopentane (**1**; δ 0 ± 2 p.p.m.) resonates at lower field than the acyclic analogue, diethyldiphenyltin (δ −66 ± 2 p.p.m.), whereas the distannacyclodecane (**2**; δ −74 ± 2 p.p.m.), shows a normal chemical shift.

In the dimer (**2**), the ring carbon atoms are related unsymmetrically to the two tin atoms, and the ^{13}C resonance from those β to tin therefore shows two sets of satellites with $J(^{119}\text{Sn}-^{13}\text{C})$ 19 and 38 Hz. Other work on acyclic compounds suggests that correct signs[8,9] and assignments[10] are $^{2}J(^{119}\text{Sn}-^{13}\text{C}) = +19$ Hz and $^{3}J(^{119}\text{Sn}-^{13}\text{C}) = -38$ Hz and we have confirmed by selective double resonance that the sign of $^{2}J(^{119}\text{Sn}-^{13}\text{C})$ in 1,1-diphenylstannacyclohexane is positive. In the monomer (**1**), the β-^{13}C nuclei in the ring are associated with a single ^{119}Sn nucleus, but there are available a two and a three-bond path for the electron-mediated coupling.

On the basis of the additive relationship $^{2/3}J(^{119}\text{Sn}-^{13}\text{C}) = {}^{3}J(^{119}\text{Sn}-^{13}\text{C}) + {}^{2}J(^{119}\text{Sn}-^{13}\text{C})$ the observed coupling constant should be about $-38 + 19 = -19$ Hz and indeed the $^{13}\text{C}_\beta$ resonance has a single pair of satellites with $^{2/3}J = -19{\cdot}6$ Hz. The quantitative agreement is fortuitous because we have ignored the dependence of ^{2}J and ^{3}J on factors such as orbital hybridization and the stereochemical relationship between the nuclei, but nonetheless, this picture does account satisfactorily for the observed sign variations.

Electron diffraction studies on cyclodecane[11] and *X*-ray investigations of its crystalline derivatives[12] have shown that the C_{10} ring has the 'boat–chair–boat' structure (Figure 1) which can be regarded as a distorted fragment of the diamond structure,[13] and in which three types of carbon atom labelled I, II, and III can be distinguished. Hydrogen atoms on carbons of types I and III approach within the van der Waals distance above the 'boats,' but the hydrogens on carbons of type II are directed away from the ring.

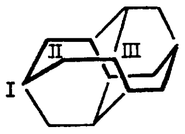


FIGURE 1. The 'boat–chair–boat' structure of cyclodecane as part of the diamond structure.

We have determined the structure of 1,1,6,6-tetraphenyl-1,6-distannacyclodecane by single-crystal Cu-K_α *X*-ray diffraction to a refinement of $R = 4{\cdot}4\%$ in space group $P2_1/c$. We find that the above general structure is preserved, the Ph_2Sn groups occupying type II positions where they are less sterically congested (Figure 2). The two 'halves' of the molecule are related by a centre of symmetry, and adjacent molecules show normal van der Waals contacts. Within the ring, the average C–C–C angle is 114°, compared with *ca.* 116·5° in the C_{10} ring, and the C–Sn–C angle is 113·3° compared with 116·9° at C(II) in the parent. The C–Sn bond-lengths are all normal at 2·15 Å compared with 1·54 Å for the C–C bond lengths in the C_{10} ring, and this has the effect of increasing the transannular separation of hydrogen atoms from 1·85 to 2·23 Å, which is to be compared with the van der Waals separation of *ca.* 2·4 Å.†

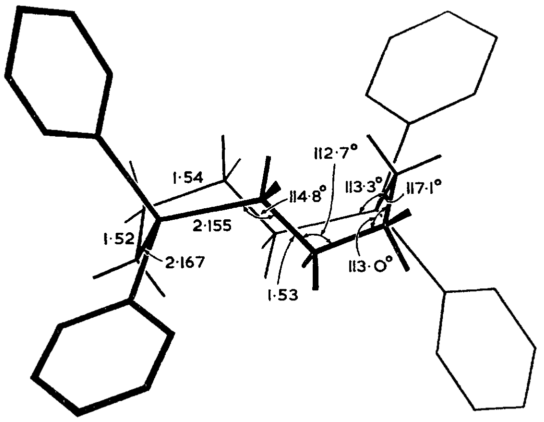


FIGURE 2. The molecular structure of 1,1,6,6-tetraphenyl-1,6-distannacyclodecane; bond length in Å.

This structure contains four types of carbon atom, but the ^{13}C n.m.r. spectrum of the solution showed only two signals. Similarly cyclodecane in solution shows one rather than three ^{13}C n.m.r. signals. Apparently in solution at room temperature, both compounds undergo rapid interconversion between the various possible conformers.

We thank the S.R.C. for support, and the International Tin Research Council for the award of a Fellowship (to M.-W.T.).

(*Received, 7th June* 1978; *Com.* 598.)

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† The atomic co-ordinates for this work 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 this communication.

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