

## Structure of 2,2-Dibutyl-1,3,2-dioxastannolane in the Solid State†

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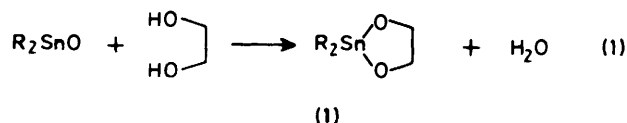
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The structure of 2,2-dibutyl-1,3,2-dioxastannolane has been determined by single-crystal X-ray diffraction. Dioxastannolane units are associated into an infinite ribbon polymer, in which the tin is surrounded by two carbon atoms and four oxygen atoms in a highly distorted octahedral arrangement. Within each unit the average Sn–O bond length is 2.04(1) Å, and between each unit it is 2.51(1) Å. The endocyclic O–Sn–O angle is 79.0(5)°, and the exocyclic C–Sn–C angle is 138.6(6)°. The Mössbauer spectra of this compound and of related glucose and mannose derivatives are reconciled with their structures. In the mannose derivative, overlapping signals can be distinguished for the five- and six-co-ordinate tin atoms in the ratio of 3:2. In solution and in the solid state, the <sup>119</sup>Sn n.m.r. spectrum of 2,2-dibutyl-1,3,2-dioxastannolane shows δ –189 and –230 respectively, indicative of the change from five- to six-co-ordination.

1,2-Diols react readily with dialkyltin oxides under conditions of azeotropic dehydration [equation (1)]<sup>1,2</sup> and the cyclic

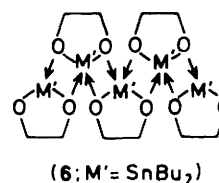
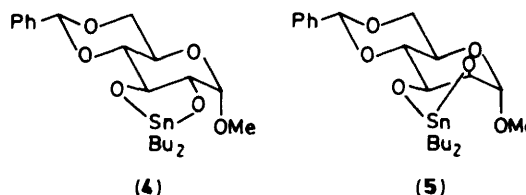
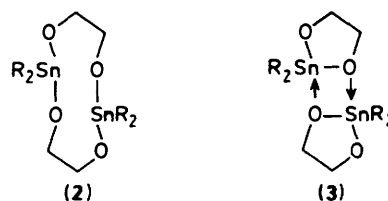


dialkoxides (dioxastannolanes) (1) which are formed have attracted a lot of attention because of their interesting structural features, and their application in organic synthesis,<sup>3</sup> particularly in carbohydrate chemistry. Measurements of molecular weight in solution show that the products are usually dimeric,<sup>1,2,4,5</sup> and this has been interpreted in terms of either the tetra-oxadistannacyclodecane structure (2) or the co-ordination dimer (3). The high-field <sup>119</sup>Sn n.m.r. chemical shifts unambiguously favour structure (3) containing five-co-ordinate tin.<sup>6</sup> The presence of the five-membered ring is supported by the single-crystal X-ray diffraction studies which are now available, though extrapolation from the solution to the solid phase must be viewed with caution because it appears that many organotin compounds become more highly associated as they solidify.

Two crystallographic studies have recently been reported. In 1979 David *et al.*<sup>7</sup> showed that the glucose derivative (4) has a dimeric structure of the type shown in (3), and in 1983, Kruger and his colleagues<sup>8</sup> showed that the corresponding mannose derivative (5) had a pentameric structure containing two five-co-ordinate tin atoms and three six-co-ordinate tin atoms as illustrated in (6). These structures are discussed in more detail below.

Mössbauer spectroscopy has also been used to investigate the structures of the dioxastannolanes in the solid state.<sup>6,9</sup> The magnitude of the quadrupole splitting shows that the co-ordination number is greater than 4, but it cannot differentiate satisfactorily between five- and six-co-ordination.

We, and others, have made previous unsuccessful attempts to determine the structure of 2,2-dibutyl-1,3,2-dioxastannolane (7), the parent member of the series, by single-crystal X-ray diffraction. In a further attempt we have now been successful,



and the results are presented here, together with some Mössbauer and <sup>119</sup>Sn n.m.r. measurements.

### Discussion

**X-Ray Crystallography.**—Two views of the structure of the compound are shown in Figure 1; the bond lengths, interbond angles, and least-square planes and atomic co-ordinates are listed in Tables 1–3. Preliminary details have been given in a previous note.<sup>10</sup>

Individual dioxastannolane units are linked together to form an infinite ribbon polymer. Within the dioxastannolane ring, the endocyclic angle O(1)–Sn–O(2) is 79.0(5)° and the exocyclic angle C(3)–Sn–C(7) is 138.6(6)°. The association places the tin in a severely distorted octahedral environment, where the angle O(2b)–Sn(1)–O(1a) is 149.0(6)°; the average Sn–O bond length within the dioxastannolane rings is 2.04(1) Å, and between the rings it is 2.51(1) Å. The rings are in a half-chair conformation,

† Supplementary data available (No. SUP 56386, 2 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii–xx. Structure factors are available from the editorial office.

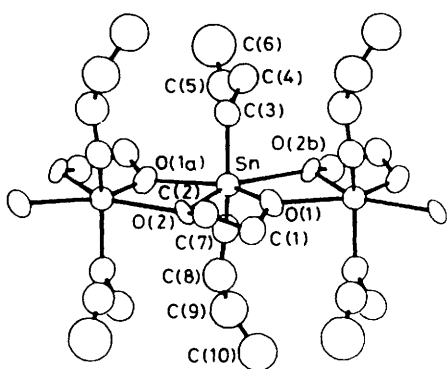


Figure 1. Structure of 2,2-dibutyl-1,3,2-dioxastannolane (7),

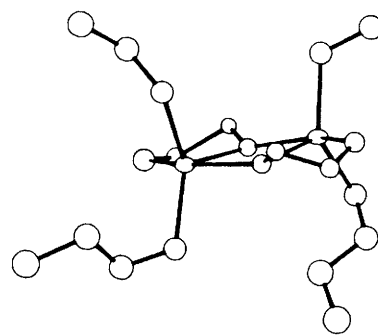


Figure 2. Structure of the glucose derivative (4)<sub>2</sub>

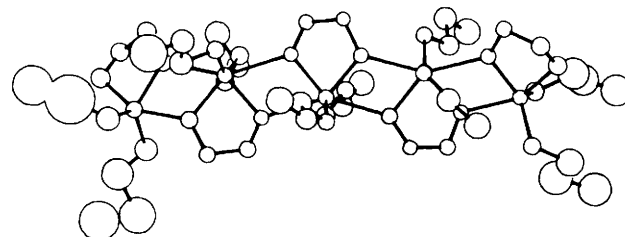
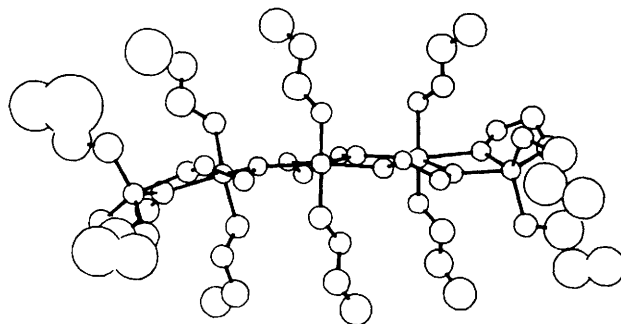
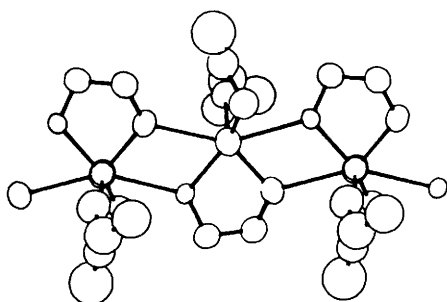


Figure 3. Structure of the mannose derivative (5)<sub>5</sub>

Table 1. Bond lengths (Å) and bond angles (°) for compound (7)

|            |           |           |           |
|------------|-----------|-----------|-----------|
| O(1)-Sn    | 1.975(14) | O(1a)-Sn  | 2.495(15) |
| O(2)-Sn    | 2.097(10) | O(2b)-Sn  | 2.520(11) |
| C(3)-Sn    | 2.128(24) | C(7)-Sn   | 2.136(22) |
| C(1)-O(1)  | 1.458(23) | C(2)-C(1) | 1.527(27) |
| O(2)-C(2)  | 1.432(17) | O(4)-C(3) | 1.528(27) |
| C(5)-C(4)  | 1.363(25) | C(6)-C(5) | 1.535(42) |
| C(8)-C(7)  | 1.381(32) | C(9)-C(8) | 1.497(36) |
| C(10)-C(9) | 1.569(36) |           |           |

|                 |           |                |           |
|-----------------|-----------|----------------|-----------|
| O(2)-Sn-O(1)    | 79.0(5)   | O(1a)-Sn-O(1)  | 144.2(6)  |
| O(2b)-Sn-O(1)   | 66.8(6)   | O(1a)-Sn-O(2)  | 65.2(6)   |
| O(2b)-Sn-O(2)   | 145.7(6)  | O(2b)-Sn-O(1a) | 149.0(6)  |
| C(3)-Sn-O(1)    | 99.4(8)   | C(3)-Sn-O(2)   | 106.4(7)  |
| C(3)-Sn-O(1a)   | 87.8(8)   | C(3)-Sn-O(2b)  | 83.4(8)   |
| C(7)-Sn-O(1)    | 112.5(8)  | C(7)-Sn-O(2)   | 105.1(7)  |
| C(7)-Sn-O(1a)   | 80.3(8)   | C(7)-Sn-O(2b)  | 86.3(8)   |
| C(7)-Sn-C(3)    | 138.6(6)  | C(1)-O(1)-Sn   | 114.8(10) |
| C(2)-C(1)-O(1)  | 108.7(18) | O(2)-C(2)-C(1) | 103.2(14) |
| C(2)-O(2)-Sn    | 112.9(9)  | C(4)-C(3)-Sn   | 125.8(14) |
| C(5)-C(4)-C(3)  | 110.5(21) | C(6)-C(5)-C(4) | 112.8(26) |
| C(8)-C(7)-Sn    | 117.8(15) | C(9)-C(8)-C(7) | 119.8(20) |
| C(10)-C(9)-C(8) | 119.1(20) |                |           |

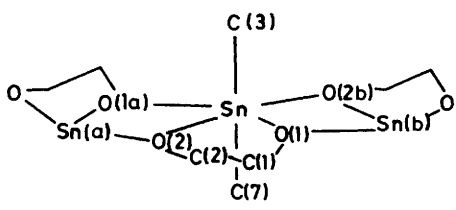
Key to symmetry operations relating designated atoms to reference atoms at (x,y,z): (a) 2.0 - x, -0.5 + y, 0.5 - z; (b) 2.0 - x, 0.5 + y, 0.5 - z.

with the two carbon atoms displaced to either side of the mean plane.

It is instructive to compare this structure with that of the glucose and mannose derivatives (4) and (5). Figures 2 and 3 show similar elevations of these two molecules, plotted from the

atomic co-ordinates given in refs. 7 and 8. For clarity, only the dioxastannolane moieties are represented, and the rest of the carbohydrate structures have been omitted.

Kruger and co-workers<sup>8</sup> have pointed out how the varying

**Table 2.** Least-squares planes with deviations of atoms in Å and angles in °


| Atom  | Plane    |          |          |          |          |      |        |
|-------|----------|----------|----------|----------|----------|------|--------|
|       | 1        | 2        | 3        | 4        | 5        | 6    | 7      |
| Sn    | 0.3951*  | 0.0357*  | -0.4097* | -0.2355* | 0.2634*  | 0.0* | 0.0*   |
| O(1)  | 0.1305*  | 0.1006*  | -0.4861* |          | -0.0452* |      | 0.0*   |
| C(1)  | -0.4713* | -0.2402* |          |          |          |      | -0.212 |
| C(2)  | 0.0532*  | 0.2923*  |          |          |          |      | 0.471  |
| O(2)  | -0.1572* | -0.1884* |          | -0.3621* | -0.2413* |      | 0.0*   |
| O(1a) | -0.0674* |          |          | 0.2536*  | -0.1269* |      | -4.590 |
| O(2b) | 0.1171*  |          | 0.6066*  |          | 0.1500*  |      | -4.176 |
| C(3)  |          |          |          |          |          | 0.0* | 2.050  |
| C(7)  |          |          |          |          |          | 0.0* | -1.898 |
| Sn(a) |          |          |          | 0.3441*  |          |      |        |
| Sn(b) |          |          | 0.2892*  |          |          |      |        |

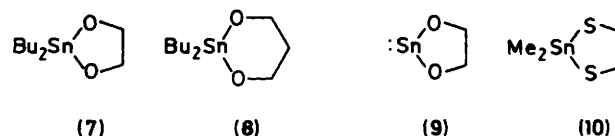
  

|                                  |       |  |       |
|----------------------------------|-------|--|-------|
| Angles between normals to planes |       | Angles between lines and normals to planes |       |
| 2-3                              | 18.50 | Plane 5 normal and line Sn-C(3)            | 2.85  |
| 2-4                              | 22.96 | Plane 5 normal and line Sn-C(7)            | 41.45 |
| 5-6                              | 88.16 |  |       |

Atoms defining plane are indicated by asterisks. Key to symmetry operations: (a)  $2.0 - x, -0.5 + y, 0.5 - z$ ; (b)  $2.0 - x, 0.5 + y, 0.5 - z$ .

**Table 3.** Fractional atomic co-ordinates ( $\times 10^4$ )

| Atom  | x          | y         | z         |
|-------|------------|-----------|-----------|
| Sn    | 10 534(1)  | 2 561(2)  | 2 565(1)  |
| O(1)  | 8 731(15)  | 830(15)   | 2 404(10) |
| C(1)  | 7 274(23)  | 1 606(25) | 2 110(13) |
| C(2)  | 7 027(20)  | 3 519(25) | 2 357(12) |
| O(2)  | 8 631(11)  | 4 311(12) | 2 295(8)  |
| C(3)  | 10 523(21) | 2 518(23) | 3 551(11) |
| C(4)  | 11 956(24) | 1 929(29) | 3 965(13) |
| C(5)  | 13 396(25) | 2 688(29) | 3 768(14) |
| C(6)  | 14 600(32) | 3 070(34) | 4 302(22) |
| C(7)  | 12 284(21) | 2 659(25) | 1 825(11) |
| C(8)  | 11 693(26) | 2 930(31) | 1 231(16) |
| C(9)  | 12 802(29) | 2 617(32) | 687(17)   |
| C(10) | 12 161(27) | 1 438(34) | 132(17)   |



compounds are compared in Table 4. It will be seen that the dioxastannolane units have a very similar geometry whether the tin is five- or six-co-ordinate, except that the exocyclic C-Sn-C angle is about  $138^\circ$  at six-co-ordinate tin in the glycol and mannose compounds, and about  $126^\circ$  at the five-co-ordinate tin in the mannose derivative. In the glucose dimer, in which the tin atoms are considered to be five-co-ordinate, the two C-Sn-C angles are different,  $139$  and  $126^\circ$ . However, the locations of the carbon atoms of the butyl groups are not well defined, and too much reliance should not be placed on the angle values. Moreover, it should be noted that the co-ordination of the tin atoms is approaching six-fold, since Sn...O contacts of ca.  $3.3$  Å occur to the O(4) atoms of the sugar moiety.

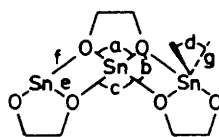
The intramonomer Sn-O bond lengths lie between  $1.98(1)$  and  $2.13(8)$  Å in all three structures (4)<sub>2</sub>, (5)<sub>5</sub>, and (7)<sub>x</sub>. The intermonomer Sn-O bond lengths show a somewhat larger variation; in the glycol and mannose derivatives they are  $2.50(2)$  and  $2.52(1)$  Å, and  $2.43$ – $2.60(?)$  Å respectively between the two six-co-ordinate tin atoms, whereas in the mannose compound they are  $2.23$ ,  $2.27(?)$  Å between five- and six-co-ordinate tin, and in the glucose compound they are  $2.17(7)$  and  $2.29(7)$  Å between two five-co-ordinate tin atoms.

Further interesting comparisons can be made with the structures of compounds (8)–(10). Pommier *et al.*<sup>13</sup> have reported preliminary results of an X-ray diffraction study of the dibutyltin derivative of propane-1,3-diol, (8). This has the structure of a ribbon polymer, similar to that of our dioxastannolane; there is trigonal-bipyramidal geometry about the

degree of association between these three dioxastannolanes can elegantly be accounted for in terms of steric interaction between the sugar residues. In the glucose derivative, the pyranose units lie in the plane of the dimeric unit, and protect the tin from further association. In the mannose derivative the pyranoside units project perpendicularly from this plane, and allow the association to proceed as far as a pentamer. In our dioxastannolane no such pendant group is present, and there is no steric hindrance to infinite polymerisation.

This tendency towards association is less marked in the acyclic dialkyltin dialkoxides, and it appears that incorporation of the OSnO unit into a small ring enhances the Lewis-acid character of the metal. This can be rationalised in terms of the relief of angle strain in the ring as the hybridisation changes from  $sp^3$  to  $sp^3d$ , and the strain-free angle at the metal relaxes from  $109^\circ$  in the tetrahedron to about  $90^\circ$  between apical and equatorial positions in the trigonal bipyramid.<sup>7,11,12</sup>

Some of the bond lengths and bond angles in these three

**Table 4.** Comparison of bond lengths and angles around tin atoms in dioxastannolanes

| Bond length/Å<br>or angle/° | Co-ordination<br>of tin | Dioxastannolane  |  |                              |
|-----------------------------|-------------------------|------------------|--|------------------------------|
|                             |                         | (4) <sub>2</sub> | (5) <sub>5</sub>   | (7) <sub>x</sub>             |
| Intramonomer<br>O-Sn-O (a)  | 5<br>6                  | 77(4), 82(4)     | 79.1(5), 80.0(7)<br>77.6(5)—78.3(5)                      | 79.0(5)                      |
| Intermonomer<br>O-Sn-O (b)  | 5—5<br>5—6<br>6—6       | 67(2), 70(2)     | 69.6(?), 70.6(?)<br>65.5(?)—69.2(?)<br>142.0(?)—150.5(?) | 65.2(6), 66.8(6)<br>149.0(6) |
| Intermonomer<br>O-Sn-O (c)  | 6                       |                  |  |                              |
| Exocyclic<br>C-Sn-C (d)     | 5<br>6                  | 126(2), 139(2)   | 124.2(8), 127.4(13)<br>134.7(9)—142.7(8)                 | 138.6(6)                     |
| Intramonomer<br>Sn-O (e)    | 5<br>6                  | 2.13(8), 2.09(8) | 2.02(4)—2.07(5)<br>2.06(5)—2.13(5)                       | 1.98(1), 2.10(1)             |
| Intermonomer<br>Sn-O (f)    | 5<br>6                  | 2.29(7), 2.17(7) | 2.23(?)—2.27(?)<br>2.43(?)—2.60(?)                       | 2.50(2), 2.52(1)             |
| Exocyclic<br>Sn-C (g)       | 5<br>6                  | 2.23(4), 2.26(4) | 2.04(3)—2.25(3)<br>2.14(4)—2.20(7)                       | 2.13(2), 2.14(2)             |

tin, with an intramonomer Sn—O bond length of 2.05(?) Å, and an intermonomer Sn—O bond length of 2.57(?) Å.

The tin(II) derivative of ethane-1,2-diol, (9), has also been investigated.<sup>14</sup> The dioxastannolane rings [Sn—O 2.07(2) and 2.11(1) Å] are associated in a three-dimensional network, with intermolecular Sn—O bond lengths of 2.31(2) and 2.34(2) Å. Each tin atom is bonded to two oxygen atoms in neighbouring glycol units, so that the tin is at the apex of a square-based pyramid with two long and two short bonds, and an apically directed unshared electron pair.

Finally, the structure of 2,2-dimethyl-1,3,2-dithiastannolane (10) has recently been reported.<sup>15</sup> Preliminary evidence had indicated that the tin was four-co-ordinate,<sup>16</sup> but the individual rings have now been shown to be associated into a zigzag polymer.<sup>15</sup> One of the two sulphur atoms bridges apical positions in a distorted trigonal bipyramid in which the endocyclic S—Sn—S bond angle is 89.55(3)°, the C—Sn—C bond angle is 121.73(18)°, the intramonomer Sn—S lengths are 2.415(1) and 2.474(1) Å, and the intermonomer Sn—S bond length is 3.182(1) Å.

**Mössbauer Spectra.**—Mössbauer spectroscopy has been used in two principal ways to investigate the structures of organotin(IV) compounds.<sup>17</sup> First, the values of the isomer shift ( $\delta$ ) and quadrupole splitting ( $\Delta E_Q$ ) give information about the co-ordination polyhedron surrounding the tin atom. Certain ranges of  $\Delta E_Q$  may be associated with particular stereochemistries, namely tetrahedral  $\text{SnR}_2\text{X}_2$ , 1.00—2.40  $\text{mm s}^{-1}$ , trigonal bipyramidal  $\text{cis-SnR}_2\text{X}_3$ , 3.0—3.5  $\text{mm s}^{-1}$ , octahedral  $\text{cis-SnR}_2\text{X}_4$ , ca. 2  $\text{mm s}^{-1}$ , and octahedral  $\text{trans-SnR}_2\text{X}_4$ , ca. 4  $\text{mm s}^{-1}$ .

However, most compounds will have structures which deviate more or less from these regular polyhedra, and the expression in equation (2) has been derived<sup>18</sup> to predict the

$$|\Delta E_Q| = 4(S)(1 - 3\sin^2\theta\cos^2\theta)^{\frac{1}{2}} \quad (2)$$

dependence of the quadrupole coupling on the value of the angle  $\theta$  which equals  $(180 - \text{angle RSnR})/2$ ; (S) is the partial

quadrupole coupling of the alkyl groups, and is taken to be  $-1.03 \text{ mm s}^{-1}$ . As the angle RSnR varies from 180 to 90°,  $\Delta E_Q$  changes smoothly from 4.12 to 2.06  $\text{mm s}^{-1}$  according to this equation, and it is therefore not possible from the quadrupole-splitting parameter alone to distinguish between a trigonal-bipyramidal and an octahedral structure.

The second sense in which Mössbauer spectroscopy has been used to provide information about the structures of organotin(IV) compounds involves the temperature dependence of the recoil-free fraction. If  $A$  is the intensity of the absorption at a particular temperature  $T$  in K, a plot of  $\ln[A(T)/A(78)]$  against  $T$  will give a straight line, the slope of which will be less for a polymer than for its monomer.<sup>19</sup>

However, Herber *et al.*<sup>9</sup> have recently reported a temperature-dependent Mössbauer study of the dioxastannolanes in which they obtained similar isomer shifts and quadrupole-splitting parameters for 2,2-dibutyl-1,3,2-dioxastannolane as the neat solid or as a frozen 0.06 mol  $\text{dm}^{-3}$  solution in butylbenzene. In solution, the dioxastannolane is accepted to exist principally as the dimer, and they concluded that this and other dioxastannolanes were dimeric also in the solid state. Our work shows that the solid is a polymer, and it must be concluded that either Mössbauer spectroscopy cannot distinguish between the five- and six-co-ordinate structures, or that polymerisation of the dioxastannolane occurs as the solution freezes.

The temperature dependence of the recoil-free fraction in six dioxastannolanes was found to correlate with their monomeric molecular weights, and this was taken as further evidence that these compounds were not polymeric in the solid state. The values of  $\text{dln}[A(T)/A(78)]/\text{dT}$  lay in the region of  $-1.3 \times 10^{-2}$  to  $-1.8 \times 10^{-2} \text{ K}^{-1}$ , which is indeed appropriate for small molecules.<sup>19</sup> This emphasises again that great caution must be exercised in the interpretation of Mössbauer data.

We have recorded the Mössbauer spectra of the compounds discussed in this paper, and our results, together with those of other workers, are listed in Table 5. Values of the quadrupole splitting predicted by Sham and Bancroft's equation<sup>18</sup> from the crystallographically determined bond angles RSnR are included. With one exception, the predicted and observed values

**Table 5.** Mössbauer parameters for 1,3,2-dioxastannolanes and related compounds

| Compound          | Co-ordination number | Angle C-Sn-C (°)   | Mössbauer parameters (mm s <sup>-1</sup> ) |                 |                                    | Ref. |
|-------------------|----------------------|--------------------|--|-----------------|------------------------------------|------|
|                   |                      |                    | Found <sup>a</sup>                         |                 | Calc. <sup>b</sup> ΔE <sub>Q</sub> |      |
|                   |                      |                    | δ  | ΔE <sub>Q</sub> |                                    |      |
| (4) <sub>2</sub>  | 5                    | 126, 139           | 1.13                                       | 2.72            | 2.94, 3.39                         | c, d |
|                   |                      |                    | 1.38                                       | 2.78            |                                    |      |
| (5) <sub>5</sub>  | 5                    | 125.8              | 1.15                                       | 2.38            | 2.93                               | c, f |
|                   |                      |                    | 6  | 137.9           |                                    |      |
| (7) <sub>4</sub>  | 6                    | 138.6              | 1.18                                       | 3.00            | 3.38                               | c    |
|                   |                      |                    | 1.10                                       | 2.80            |                                    | 6    |
|                   |                      |                    | 1.18                                       | 3.15            |                                    | g    |
|                   |                      |                    | 1.212                                      | 2.931           |                                    | 9    |
|                   |                      |                    | 1.223                                      | 3.002           |                                    | h, 9 |
|                   |                      |                    | 1.10                                       | 2.50            |                                    | c    |
| (8) <sub>4</sub>  | 6                    | (113) <sup>i</sup> | 1.10                                       | 2.50            |                                    | c    |
| (10) <sub>4</sub> | 5                    | 121.4              | 1.50                                       | 2.60            | 2.77                               | j    |
|                   |                      |                    |  | 2.33            |                                    |      |

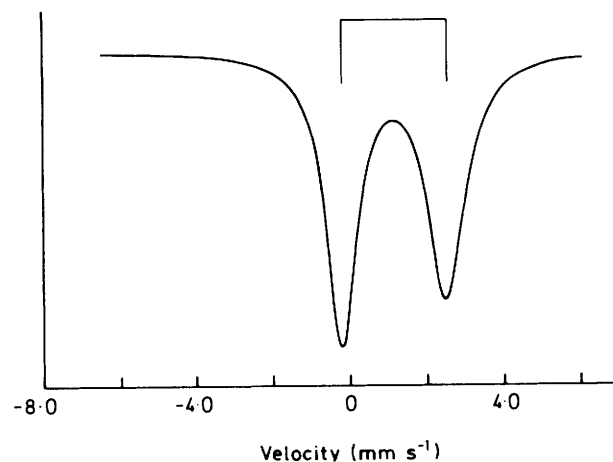
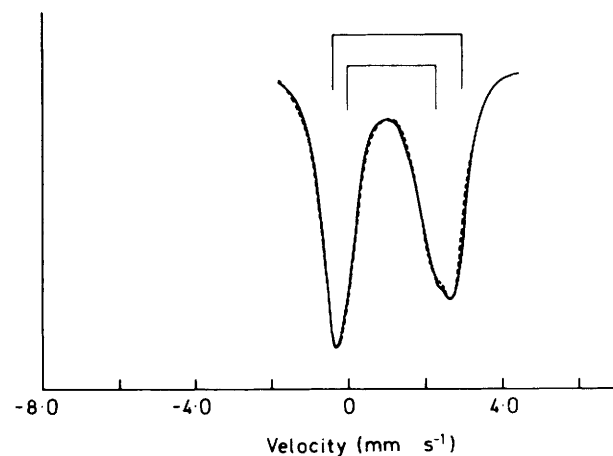
<sup>a</sup> At 77 K, referred to SnO<sub>2</sub>. <sup>b</sup> By equation (2). <sup>c</sup> Present work. <sup>d</sup> The relative linewidths might imply the presence of two overlapping doublets; see text. <sup>e</sup> D. Cunningham, personal communication. <sup>f</sup> Relative intensities 2:3, see text. <sup>g</sup> S. P. Narula, R. K. Sharma, S. Lata, N. Kapur, and R. Seth, *Indian J. Chem., Sect. A*, 1983, **22**, 248. <sup>h</sup> Frozen solution, 0.06 mol dm<sup>-3</sup> in BuPh. <sup>i</sup> Calculated from the Mössbauer parameters by use of equation (2). <sup>j</sup> M. A. Delmus, J. C. Maire, W. McFarlane, and Y. Richard, *J. Organomet. Chem.*, 1975, **87**, 285. <sup>k</sup> L. M. Epstein and D. K. Straub, *Inorg. Chem.*, 1965, **4**, 1551.

of ΔE<sub>Q</sub> agree within 0.4 mm s<sup>-1</sup>, and the equation does appear to have some value in the analysis of Mössbauer data.

The spectra of the glucose derivative (4)<sub>2</sub> and of the mannose derivative (5)<sub>5</sub> merit some comment. The crystal structure of (4)<sub>2</sub> shows surprisingly that the two C-Sn-C angles in the dimer (Figure 2) are different,<sup>7</sup> namely 126(2) and 139(2)°, which, by equation (2), would be expected to give rise to a pair of doublets with ΔE<sub>Q</sub> 2.94 and 3.39 mm s<sup>-1</sup>. The experimental spectrum is shown in Figure 4, and shows two absorption components with an intensity ratio of about 0.85, which remained unchanged despite repeated sample powdering. This might indicate the partial overlap of two doublets with different isomer shifts and quadrupole couplings, but the components could not be separated by the available fitting routines, and the possibility of inadequate sample randomization cannot be ruled out. In CDCl<sub>3</sub> solution the compound shows a single <sup>119</sup>Sn n.m.r. signal at -125.4 relative to SnBu<sub>4</sub>, which is characteristic of five-co-ordinate tin.<sup>7</sup>

Similarly the mannose derivative, (5)<sub>5</sub>, contains two different types of tin site. Coincidentally the C-Sn-C angles are similar to those in the glucose derivative, namely 127.4(13) and 124.2(8) (average 125.8°) at the terminal five-co-ordinate sites, and 134.7(9), 136.3(8), and 142.7(8) (average 137.9°) at the medial six-co-ordinate sites, in relative populations 2:3. The experimental spectrum is illustrated in Figure 5, and shows two features of equal area but with different amplitudes and widths, and with some indication of resolution of the broader signal. We interpret this as implying the presence of two partially overlapping doublets.

Various simulations of the spectrum were carried out. The most satisfactory was obtained by applying the constraint that the first two lines should have the same intensities, as should the second two lines. This leads to the simulated spectrum which is included in the Figure, with the parameters δ 1.27, ΔE<sub>Q</sub> 3.44, Γ 0.97, and δ 1.15, ΔE<sub>Q</sub> 2.38, Γ 0.97 mm s<sup>-1</sup> (χ<sup>2</sup> 313.0), with relative areas 3:2. The first doublet is therefore assigned to the

**Figure 4.** Mössbauer spectrum of the glucose derivative (4)<sub>2</sub>**Figure 5.** Mössbauer spectrum of the mannose derivative (5)<sub>5</sub>

six-co-ordinate tin atoms, and the second to the five-co-ordinate tin atoms in the pentamer (6). An alternative analysis with the constraint that lines 1 and 3, and lines 2 and 4, should constitute the doublets, gave the parameters δ 1.43, ΔE<sub>Q</sub> 3.12, Γ 0.98 and δ 0.89, ΔE<sub>Q</sub> 2.88, Γ 0.98 mm s<sup>-1</sup>. This gave an equally good fit with the observed spectrum (χ<sup>2</sup> 285.4), but it was rejected on the grounds that a value of δ 0.89 is unreasonably low.

<sup>119</sup>Sn N.M.R. Spectroscopy.—The <sup>119</sup>Sn n.m.r. spectra of organotin compounds in solution have been widely used as criteria of structure, the chemical shift moving upfield with increases in the co-ordination number of tin. No results have been published on solid-state <sup>119</sup>Sn spectroscopy, but a comparison between the chemical shifts in solution and the solid state would be expected similarly to show up any change of structure which might occur with solidification.

Table 6 shows the values of δ(<sup>119</sup>Sn) for 2,2-dibutyl-1,3,2-dioxastannolane (7), and, to serve as a check on the method, for tetraphenyltin, in solution, and, by magic angle spinning, in the solid state. Tetraphenyltin is tetrahedrally four-co-ordinate in both solution and the solid state, and, as would be expected, the chemical shift is essentially the same under the two conditions. On the other hand, the value of <sup>119</sup>Sn for the dioxastannolane (7) shows an upfield shift of 41 p.p.m. between the solution and solid, consistent with the change from a five-co-ordinate dimer to a six-co-ordinate polymer.

**Table 6.** Values of  $\delta(^{119}\text{Sn})$  in solution and the solid state

|                 | $\delta$               |             |
|-----------------|------------------------|-------------|
|                 | Solution               | Solid state |
| $\text{SnPh}_4$ | $-120 \pm 10^*$        | $-120.75$   |
| (7)             | $-189 (\text{CHCl}_3)$ | $-230$      |

\* Estimated; A. G. Davies, P. G. Harrison, J. D. Kennedy, T. N. Mitchell, R. J. Puddephatt, and W. McFarlane, *J. Chem. Soc. C*, 1969, 1136.

It is clear that solid-state  $^{119}\text{Sn}$  n.m.r. spectroscopy will provide a powerful method for investigating organotin structure.

### Conclusions

The propensity of the dioxastannolanes to associate in the solid state is apparently strongly dependent upon the steric demands of the substituents. Dimeric, pentameric, and polymeric structures have now been identified, but further variants will probably be discovered.

Mössbauer spectroscopy appears to be of limited use for distinguishing between these possible structures, but solid-state  $^{119}\text{Sn}$  n.m.r. spectroscopy promises to be a better tool.

In solution, these various oligomers and polymers dissociate to give mainly dimeric species, but the likelihood of higher oligomers, and of a variety of structures amongst these dimers, should not be overlooked.

### Experimental

The dioxastannolanes were prepared by azeotropic dehydration of a mixture of dibutyltin oxide and the 1,2-diol in benzene or toluene, as reported in the literature.<sup>1,2</sup> The sample of 2,2-dibutyl-1,3,2-dioxastannolane for X-ray diffraction studies was recrystallised from chloroform.

**X-Ray Crystallography.**—Crystal data.  $\text{C}_{10}\text{H}_{22}\text{O}_2\text{Sn}$ ,  $M = 292.97$ , orthorhombic,  $a = 8.103(4)$ ,  $b = 7.409(3)$ ,  $c = 21.563(4)$  Å,  $U = 1294.46$  Å<sup>3</sup>, space group  $P2_12_12_1$ ,  $Z = 4$ ,  $D_c = 1.39$  g cm<sup>-3</sup>,  $\lambda(\text{Mo-K}\alpha) = 0.71069$  Å,  $\mu(\text{Mo-K}\alpha) = 17.93$  cm<sup>-1</sup>,  $F(000) = 592$ .

A total of 1346 unique intensity data were measured to a maximum of  $25^\circ$  in  $\theta(\text{Mo-K}\alpha)$  radiation, 1011 being considered observed [ $I > 1.5\sigma(I)$ ]. Final  $R$  values were  $R = 0.069$ ,  $R' = [\sum(w\Delta)^2/\sum wF_o^2]^{1/2} = 0.076$ , weighting scheme  $w = 1/[\sigma^2(F_o) + gF_o^2]$  where  $g = 0.0005$ .

**Solution and refinement of the structure.** Intensity data were collected on a Nonius CAD4 diffractometer operating in the  $\omega-2\theta$  mode as reported previously.<sup>20</sup> Inspection of the Patterson map revealed the Sn atom to be at a position approximately 0.25 in both  $y$  and  $z$ . Development of the structure proceeded slowly with refinement of the thermal parameters acting as an indication of the expansion of the correct image of the four present. After location of the 'chelating' diol, refinement of these atoms by full-matrix least squares<sup>21</sup> and inspection of Fourier difference maps enabled atoms of the butyl chain which exhibited high thermal motion to be placed. Hydrogen atoms could not be located. All atoms were refined with anisotropic thermal parameters. Final atomic fractional co-ordinates are given in Table 3.

**Solid-state N.M.R. Spectroscopy.**—Solid-state  $^{119}\text{Sn}$  n.m.r. spectra were recorded at 111.91 MHz on a Bruker CXP 200 spectrometer with proton decoupling, cross polarisation, and magic angle spinning at ca. 3500 Hz.

**Mössbauer Spectroscopy.**—Mössbauer spectra were recorded at Birkbeck College under the University of London Intercollegiate Research Service, or at the International Tin Research Institute, and are quoted at 85 K with respect to  $\text{SnO}_2$ .

### Acknowledgements

This work was carried out by Dr. A. J. Price during the tenure of a S.E.R.C. C.A.S.E. Studentship in association with the International Tin Research Council. We are very grateful to Dr. R. Hill (International Tin Research Institute) and I. Sayer (University of London Intercollegiate Research Service) for recording and simulating the Mössbauer spectra, and to Dr. D. Gillies and Bruker Spectrospin Ltd, for recording the solid-state n.m.r. spectra. We acknowledge support from the S.E.R.C. for the provision of crystallographic and computing facilities.

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Received 3rd April 1985; Paper 5/565