Acta Cryst. (1962). **15**, 9

The Determination of Intramolecular Sn-Sn-Distances in 1,4-Di(Trimethyltin)Butane by Means of X-rays

BY H. MENDEL*

Koninklijke/Shell-Laboratorium, Amsterdam, (Shell International Research Maatschappij N.V.), The Netherlands

(*Received* 20 *March* 1961)

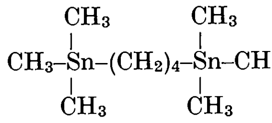
The distribution of the intramolecular Sn–Sn-distances in 1,4-di(trimethyltin)butane was determined experimentally. The results are interpreted in terms of a model consisting of two conformations each containing one gauche link.

Introduction

The method for determining order phenomena in liquids by means of X-ray diffraction, outlined in a following paper (Mendel, 1962), was used in a study of end-to-end distances in aliphatic hydrocarbons. An experimental determination of these distances affords information on the extent to which the molecules are curled up in the liquid. To get sufficiently pronounced diffraction effects it is necessary to introduce heavy atoms (Holleman, 1960). In order to retain the aliphatic character of the compounds investigated, tin in the form of trimethyltin groups was chosen for this purpose and as intramolecular distances were to be measured, such a group was introduced at each end of the molecule (α,ω-substitution).

Experimental

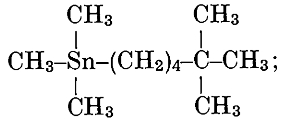
The following compounds were used in the investigation:



$CH_3\text{–}\overset{CH_3}{\underset{CH_3}{Sn}}\text{–}(CH_2)_4\text{–}\overset{CH_3}{\underset{CH_3}{Sn}}\text{–}CH_3$;

I

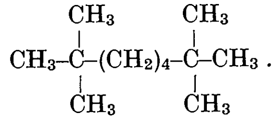
1,4-di(trimethyltin)butane



$CH_3\text{–}\overset{CH_3}{\underset{CH_3}{Sn}}\text{–}(CH_2)_4\text{–}\overset{CH_3}{\underset{CH_3}{C}}\text{–}CH_3$;

II

1(trimethyltin)-5,5′-dimethylhexane



$CH_3\text{–}\overset{CH_3}{\underset{CH_3}{C}}\text{–}(CH_2)_4\text{–}\overset{CH_3}{\underset{CH_3}{C}}\text{–}CH_3$.

III

2,2′-7,7′-tetramethyloctane

An equimolar mixture of I and III has exactly the same mole fraction for all atoms as II; the only difference between the mixture and II will be—to a first approximation—the intramolecular Sn–Sn-distances. Thus subtraction of the two distribution functions gives information about these latter distances, which one expects to find at about 7 Å (see Table 4). A check on the reliability of this difference-distribution function $\Delta\sigma_M(r)$ is its behaviour at r-values equal to the bonding distances of atoms. Up to the largest bonding distance (Sn–C = 2·2 Å) the difference curve $\Delta\sigma_M(r)$ has to be zero as in both samples both frequency and weight of the bonding distances are exactly equal.

As the determination of the difference curve $\Delta\sigma_M(r)$ entails taking the difference of a difference, relative small errors in the distribution curves $\sigma_M(r)$ can exert a very large influence indeed in $\Delta\sigma_M(r)$. It was therefore felt to be advisable to scale the intensities of the two samples relative to each other. The denominators in the expressions of the scaling factor (ref. 1, equation (14)) are equal, and so

$$\alpha' = \Sigma s^2 I_{\text{exp.}}(\text{mixture}) / \Sigma s^2 I_{\text{exp.}}(\text{mono-tin compound}) .$$

As the smallest possible intramolecular Sn–Sn-distance is ~ 4 Å, α' has to converge at $s > 2$ because for smaller interatomic vectors the two samples are identical. As shown in Table 1, good convergence is obtained, and the problem left is the determination of the absolute scale, which can only be carried out if the atomic scattering curves of the constituent atoms are known very accurately. This is so for carbon and hydrogen, but for tin the most recent data, calculated by Thomas & Umeda (1957), are based on

Table 1. *Convergence of relative scaling factor*

s	α'
1·5	1·04
2·–	1·05
2·5	1·05
3·–	1·05

---

* Present address: Unilever Research Laboratory, Vlaardingen, The Netherlands.

a model which is inadequate for our purpose. Recent calculations of MacGillavry (1960) for silver show a systematic deviation from the Thomas & Umeda data. Therefore a corrected atomic scattering curve for tin was used, obtained by multiplying that of Thomas & Umeda by the ratio of the two silver curves.

Table 2
Convergence of scaling factor for mono-tin compound

s	α
4·0	0·714
4·5	0·706
5·0	0·701
5·5	0·695
6·0	0·687
6·5	0·684
7·–	0·691

Table 3
Convergence of scaling factor for mixture

s	α
4·0	0·765
4·5	0·765
5·0	0·766
5·5	0·764
6·0	0·758
6·5	0·754
7·–	0·756

Reasonable convergence of the scaling factor α is obtained as can be judged from Table 2 for the mono-tin compound II and in Table 3 for the mixture. Now the absolute scale of the difference curve $\Delta\sigma_M(r)$ can be determined (and the curve itself put on an absolute scale by a simple multiplication).

Results and discussion

The difference curve $4\pi\Delta\sigma_M(r)/r$, on an absolute scale, is given in Fig. 1. As can be seen, it is practically zero up to r-values of 2 Å (as it should be) and then shows a very clear maximum between 5·3 and 7·8 Å. If the assumption is made that this maximum is only due to Sn–Sn-distances, then by a comparison of the experimentally determined area and the theoretically calculated one, the percentage of tin can be found. This proved to be 52%, in good—although indubitably partly fortuitous—agreement with the expected value of 50%. The minimum between 2 and 5 Å must be due to a disappearance of non-bonding distances. An explanation in terms of a model has not been attempted for this minimum.

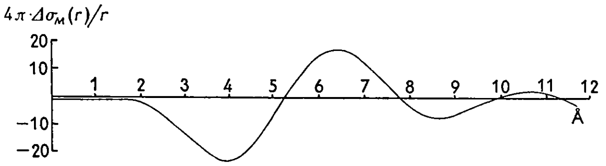


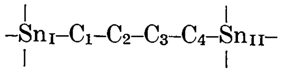
Fig. 1. Difference curve $4\pi\Delta\sigma_M(r)/r$ between a mixture of 1,4-di(trimethyltin) butane +2,2′,7,7′-tetramethyloctane and 1-(trimethyltin)-5,5′-dimethylhexane at 20 °C.

If the above assumption, namely that the maximum is only due to Sn–Sn-distances, is retained, an interpretation in terms of a model is possible. It was further postulated that only trans and gauche configurations occur and the Sn–Sn-distances were calculated for all configurations for which this distance exceeds 5 Å.

Table 4. *End-to-end distance for various configurations*

Configuration	Sn–Sn-distance
All trans	7·6 Å
C_4–Sn_{II} gauche	5·9
C_3–C_4 gauche	7·0

These configurations and the corresponding distances are given in Table 4, where the numbering of the atoms is as in Fig. 2. It follows directly from the difference curve (Fig. 1), that the most probable conformations are those with one gauche link in the chain, whereas the all-trans configuration can practically be excluded. The two different conformations with one gauche link in the chain and Sn–Sn-distances of 5·9 and 7·0 Å, respectively, account, in first approximation, very well for the observed maximum in the difference curve. Owing to the limited amount of intensity data—only up to $s=2·5$—no great resolving power can be obtained and so one broad maximum with its peak value between 6 and 7 Å is all that can be expected.



$$-Sn_I-C_1-C_2-C_3-C_4-Sn_{II}-$$

Fig. 2. Numbering of atoms.

It can therefore be concluded that these molecules in the liquid state are not straight but curled up to a certain extent.

The author wishes to thank Dr W. C. B. Smithuysen for the samples of the tin compounds and Miss I. Kerker for doing most of the experimental work and for her assistance in the calculations.

References

Holleman, Th. (1960). *Rec. Trav. Chim. Pays-Bas*, **79**, 1301.

MacGillavry, C. H. (1960). Private communication.

Mendel, H. (1962). *Acta Cryst.* **15** (In press).

Thomas, L. H. & Umeda, K. (1957). *J. Chem. Phys.* **26** 293.