The Si–N bond length of 1·64 (1) Å is significantly shorter than the 'short' Si–N distances in the range 1·72–1·74 Å found in $(H_3Si)_2N$– and $[(CH_3)_3Si]_2N$– derivatives, and appears to be the shortest Si–N bond length reported for a stable compound [very similar anion dimensions have recently been found in $Eu\{N[Si(CH_3)_3]_2\}_3$, which can also be considered to be essentially ionic (Hursthouse, 1973)]. The formal negative charge on nitrogen should favour delocalization of its lone pairs; it appears that this delocalization has taken place into bonding orbital(s), which is certainly consistent with some degree of $p\pi$–$d\pi$ bonding in the Si–N bonds. The Si–N–Si angle of 136·3 (1·2)° is greater than those found in other disilazanes (range 118 to 129°), consistent with spectroscopic predictions (Bürger, 1973). However, the angle may also be influenced by steric factors, and it is possible that the total covalent bonding energy of the isolated molecule is relatively insensitive to the Si–N–Si angle. The mean Si–C(H_3) bond length has the typical value of 1·90 (2) Å, suggesting that there is little librational shortening of this distance, and therefore that the short Si–N bond cannot be accounted for by libration.

The calculations were performed on the Cambridge University Titan and IBM 370/165 computers with programs written by G.M.S.

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Trimethyltin Methoxide

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Abstract. $(CH_3)_3SnOCH_3$, orthorhombic, $P2_12_12_1$, $a=6{\cdot}61$ (1), $b=8{\cdot}10$ (5), $c=12{\cdot}61$ (2) Å, $U=675$ Å^3, $Z=4$, $D_x=1{\cdot}92$ g cm^{-3} at -55 °C. Approximately planar trimethyltin groups are linked by methoxide units to form infinite zigzag -O–Sn–O–Sn– chains along the y (needle) axis, with trigonal bipyramidal coordination of tin. Mean bond lengths and angles are: Sn–C 2·14 (2); Sn–O 2·23 (3); O–C 1·43 (3) Å; O–Sn–O′ 172·4 (7); Sn–O–Sn′ 131·2 (12)°. The structure was refined to an R of 0·057 for 1106 unique observed reflexions obtained at about -55 °C with a two-circle diffractometer.

Introduction. X-ray crystallographic studies have established the presence of approximately symmetrical hydroxide bridging in a number of organotin compounds. This results in dimeric molecules in dimethyltin hydroxide nitrate (Domingos & Sheldrick, 1974*a*), and in polymeric structures in $(CH_3)_3SnOH$ (Kasai, Yasuda & Okawara, 1965), $(CH_3)_3SnNCO.(CH_3)_3SnOH$ (Hall & Britton, 1972) and $[(CH_3)_3Sn]_3(OH)CrO_4$ (Domingos & Sheldrick, 1974*b*). Chapman, Davies, Harrison & McFarlane (1970) have proposed a methoxide-bridged dimeric structure for dimethyltin methoxide chloride on the basis of infrared, Mössbauer, n.m.r. and molecular-weight measurements. We report here the determination of the structure of a crystal which we obtained from a preparation of dimethyltin dimethoxide, although the structure determination shows unambiguously that it was trimethyltin methoxide. The crystals were found to sublime rapidly out of the X-ray beam at room temperature, so the intensities were collected at about -55 °C on a Stoe computer-controlled two-circle diffractometer modified for low-temperature operation.

Experimental. Dimethyltin dimethoxide was prepared by the reaction of dimethyltin dichloride with sodium methoxide in dry methanol at 0 °C (Davies & Harrison, 1967), and identified by its infrared spectrum. Since it is sensitive to hydrolysis, we removed the solvent under vacuum and attempted to grow crystals by vacuum sublimation. The temperature was progressively increased to about 120 °C, when a few needle-shaped crystals formed on the cold finger; these were sealed into Lindemann-glass capillary tubes. A suitable crystal for X-ray diffraction, of approximate dimensions $0{\cdot}12\times0{\cdot}88\times0{\cdot}11$ mm, was obtained by melting one of

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these crystals (at about 80°C) and allowing it to cool very slowly. The trimethyltin methoxide was presumably a disproportionation product which was isolated because it is more volatile than dimethyltin dimethoxide. The ease of hydrolysis and the small quantity obtained made it difficult to confirm the identity by conventional chemical methods.

Intensities were collected in an approximately constant count mode (Clegg & Sheldrick, 1974) for layers $h0l$ to $h11l$ inclusive, with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å) and a graphite crystal monochromator. 2121 reflexions were measured, of which 200 were rejected because of background imbalance or because the net count was less than 3σ based on counting statistics. Averaging equivalent reflexions led to 1106 unique observed reflexions. Although standard (zero-layer) reflexions were employed, it was found that refinement of the inter-layer scale factors led to a significant improvement in the final stages of structure refinement. Unit-cell dimensions were obtained from diffractometer measurements at about −55°C.

The tin coordinates were determined from the Patterson function, but the resulting difference synthesis did not uniquely determine the light-atom positions, probably because the special values of x/a and z/c for the tin atom imposed extra symmetry, so some trial and error was necessary. It was found possible to refine the structure into a number of chemically unacceptable false minima with R below 0·10. Two minima were found with values of $R_w = \sum w^{1/2}|F_o - F_c|/\sum w^{1/2}|F_o|$ of about 0·06, significantly lower than the rest; these were approximately related by the transformation $x' = a - x$ for all atoms except methoxide. The solution reported here does not show any systematic variations of the mean value of $w(F_o - F_c)^2$ as a function of parity group *etc.*, and has a shortest non-bonded distance of 3·04 Å. The solution rejected had a much less flat analysis of variance and was chemically unreasonable, *e.g.* the O···C(1) distance was 2·29 Å. The structure was refined by full-matrix least-squares with an anisotropic temperature factor for tin and isotropic temperature factors for the other atoms, and the weighting scheme $w = (18{\cdot}81 + |F_o| + 0{\cdot}00886F_o^2)^{-1}$. Complex neutral-atom scattering factors were employed for all atoms (Cromer, 1965; Cromer & Waber, 1965), but no significant changes in R occurred when the structure was refined as the opposite enantiomorph. The secondary extinction coefficient refined to $10^6 Q_0 r^* = 70\ (36)\ \mathrm{cm}^{-1}$ (Larson, 1970). The refinement converged to $R_w = 0{\cdot}059$, with a corresponding $R = 0{\cdot}057$; the highest peak in a final difference map was about 2·2 e Å^{-3}. Atom coordinates and temperature factors are given in Tables 1 and 2, interatomic distances and angles in Tables 3, 4 and 5.†

Table 1. *Fractional coordinates* (× 10^4) *and isotropic temperature factors* (Å^2 × 10^3)

	x/a	y/b	z/c	U
Sn	5119 (3)	3184 (1)	7597 (2)	
O	4204 (20)	5639 (11)	6902 (10)	20 (3)
C(1)	1992 (32)	2650 (21)	7831 (16)	34 (5)
C(2)	6868 (31)	2787 (18)	6190 (15)	27 (4)
C(3)	6587 (30)	4324 (18)	8948 (14)	24 (4)
C(4)	3017 (35)	5385 (25)	5971 (17)	36 (5)

Table 2. *Anisotropic temperature factors* (Å^2 × 10^3)

The anisotropic temperature factor takes the form:

$$\exp\,[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)].$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn	16 (1)	22 (5)	9 (1)	0	−3 (1)	0

Table 3. *Bond lengths* (Å)

Sn–O	2·26 (2)
Sn–O′	2·20 (2)
Sn–C(1)	2·13 (2)
Sn–C(2)	2·14 (2)
Sn–C(3)	2·17 (2)
O –C(4)	1·43 (3)

Table 4. *Bond angles* (°)

O——Sn–O′	172·4 (7)
Sn——O –Sn′	131·2 (12)
C(2)–Sn–C(1)	127·4 (9)
C(2)–Sn–C(3)	118·3 (8)
C(1)–Sn–C(3)	114·3 (8)
C(4)–O –Sn	109·9 (13)
C(1)–Sn–O	88·4 (10)
C(2)–Sn–O	87·4 (9)
C(3)–Sn–O	92·9 (9)
C(1)–Sn–O′	88·1 (9)
C(2)–Sn–O′	89·3 (9)
C(3)–Sn–O′	94·7 (9)

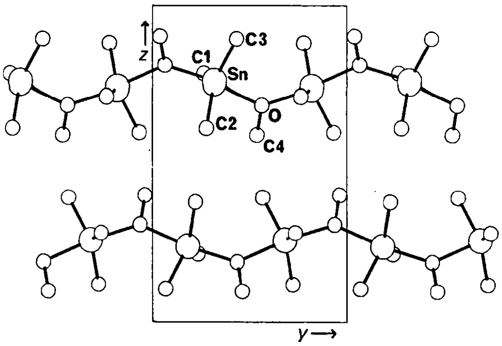

Fig. 1. Projection of the structure perpendicular to [100], with the atoms of the asymmetric unit labelled.

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† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30240 (6 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

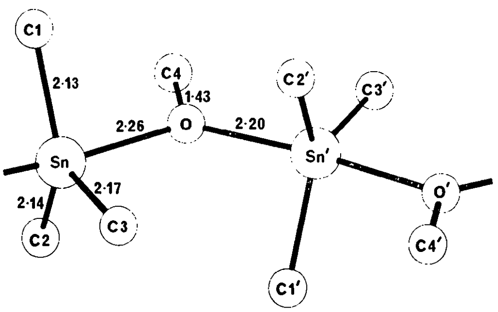

Fig. 2. The repeat unit of the chain, with bond lengths in Å.

Table 5. *Non-bonded distances* (Å) *less than* 4·1 Å

Within asymmetric unit	
Sn–C(4)	3·05
O–C(1)	3·06
O–C(2)	3·04
O–C(3)	3·21
C(1)–C(2)	3·83
C(3)–C(1)	3·61
C(3)–C(2)	3·70
C(4)–C(1)	3·30
C(4)–C(2)	3·31
First atom transformed by:	
$(1{\cdot}5-x,\ 1-y,\ z-0{\cdot}5)$	
C(3)–C(2)	3·81
$(0{\cdot}5+x,\ 0{\cdot}5-y,\ 1-z)$	
C(4)–C(2)	3·82
$(1-x,\ 0{\cdot}5+y,\ 1{\cdot}5-z)$	
Sn–Sn	4·06
Sn–C(3)	3·85
Sn–C(4)	3·15
C(1)–C(3)	3·63
C(1)–C(4)	4·07
C(1)–O	3·01
C(2)–O	3·05
C(2)–C(3)	3·62
C(2)–C(4)	4·07
C(3)–O	3·21
C(3)–C(4)	3·20
$(0{\cdot}5-x,\ 1-y,\ 0{\cdot}5+z)$	
C(4)–C(3)	3·98

Discussion. Approximately planar trimethyltin groups are linked by methoxides to form infinite zigzag -O-Sn-O-Sn- chains along the y (crystal needle) axis, with trigonal bipyramidal ($\mathrm{OC_3O}$) coordination of tin (Figs. 1 and 2). The Sn–O bond lengths are approximately equal [mean = 2·23 (2) Å], and except for the methyl groups attached to tin all the atoms in a chain lie approximately in the plane defined by:

$$5{\cdot}463x/a+0{\cdot}005y/b-7{\cdot}099z/c=-2{\cdot}591\ \text{Å}$$

(mean deviation 0·006 Å). Similar chain structures have been reported for trimethyltin hydroxide (Kasai, Yasuda & Okawara, 1965) and trimethyltin fluoride (Clark, O'Brien & Trotter, 1964), but, unlike these, trimethyltin methoxide does not exhibit disorder of the trimethyltin group, possibly because the intensities were collected at low temperature. Significantly shorter Sn–O bonds have been reported for $\mathrm{-(CH_3)_3Sn{-}O(H){-}(CH_3)_3Sn{-}}$ units in $\mathrm{(CH_3)_3SnNCO.(CH_3)_3SnOH}$ [Sn–O = 2·15 (5) and 2·14 (5) Å; Hall & Britton, 1972] and in $\mathrm{[(CH_3)_3Sn]_3(OH)CrO_4}$ [Sn–O = 2·14 (3) and 2·17 (4) Å: Domingos & Sheldrick, 1974*b*], but in these two compounds both tin atoms also make a longer bond to oxygen or nitrogen. Although the intensities were collected at low temperature for chemical reasons, the reduction in atomic thermal motion may have proved decisive in eliminating some of the false minima, and in avoiding problems of trimethyltin group disorder or rotation.

We are grateful to the Science Research Council for providing the diffractometer. The calculations were performed on the Cambridge University IBM 370/165 computer with programs written by Drs W. Clegg, W D. S. Motherwell, P. J. Roberts and G.M.S.

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