

## The Molecular Structures of Four Substituted Stannanes by Gas-Phase Electron Diffraction

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The molecular structures of  $\text{MeSnCl}_3$ ,  $\text{Me}_3\text{SnCl}$ ,  $\text{Me}_3\text{SnH}$ , and  $\text{Me}_2\text{SnH}_2$  ( $\text{Me} = \text{CH}_3$ ) have been studied by gas-phase electron diffraction. Data reduced by standard techniques are consistent with molecules in which tin is in approximately tetrahedral coordination; optimum precision was achieved by the calculation of improved complex scattering factors for tin. In  $\text{MeSnCl}_3$  and  $\text{Me}_3\text{SnCl}$ , the Sn-Cl bond lengths ( $r_g$ ) are  $2.306 \pm 0.003$  and  $2.354 \pm 0.008$  Å respectively, fitting a pattern in which length decreases as the number of chlorine substituents increases. The four molecules have Sn-C bond lengths ( $r_g$ ) of  $2.105 \pm 0.016$ ,  $2.108 \pm 0.006$ ,  $2.149 \pm 0.004$  and  $2.153 \pm 0.004$  Å respectively, demonstrating that the presence of chlorine again has a shortening effect.

### Introduction

Tin is an element whose electron-diffraction complex scattering factors have not been known accurately until recently (Beagley & McAloon, 1971). Now that reliable scattering factors are available, it has proved possible to analyse electron-diffraction sector-microdensitometer data for methyltrichlorostannane ( $\text{MeSnCl}_3$ ), trimethylchlorostannane ( $\text{Me}_3\text{SnCl}$ ), trimethylstannane ( $\text{Me}_3\text{SnH}$ ) and dimethylstannane ( $\text{Me}_2\text{SnH}_2$ ). Interest centres mainly on the Sn-C and Sn-Cl bond lengths, which are not constant in molecules of this type (Fujii & Kimura, 1971). The methylchlorostannanes have previously been studied by the visual method of electron diffraction (Skinner & Sutton, 1944).

### Experimental

#### Methyltrichlorostannane

A small sample was prepared by reacting tetramethylstannane with tetrachlorostannane in the appropriate molar ratio, and purified by vacuum sublimation. Its gas-phase electron-diffraction pattern was recorded in the Balzers electron-diffraction instrument at UMIST at a temperature of *ca.* 80°C. Diffraction rings were observed to extend to  $s \approx 26$  Å<sup>-1</sup>, so that useful intensity data were accessible from experiments using camera distances 100, 50 and 25 cm; the respective numbers of pattern diameters scanned by automated microdensitometer were 10, 12 and 14.

#### Trimethylchlorostannane

The sample was prepared by the method of Manulkin (1946) and purified by repeated vacuum sublimations. Diffraction patterns were recorded at 92°C. This temperature is near the upper limit for the gas nozzle employed, and the vacuum seals tended to leak. Hence the diffraction patterns obtained showed signs of re-

sidual gas scattering. Condensation of material in the tubes leading to the gas nozzle was overcome by auxiliary electrical heating. Diffraction rings were observed to extend only to  $s \approx 16$  Å<sup>-1</sup>, so that only the 100 and 50 cm camera distances were used for the collection of intensity data (10 and 12 diameters respectively).

#### Trimethylstannane

The sample was prepared by the reduction of trimethylchlorostannane with lithium aluminum hydride, with isoamyl ether as solvent, since dioxan (suggested by Clark, Furnival & Kwon, 1963) is of comparable volatility to the product. Separation and purification were achieved by repeated redistillation. Diffraction patterns were recorded at 0°C with a good vacuum and negligible residual gas scattering. Despite this, diffraction rings were not observed beyond  $s \approx 16$  Å<sup>-1</sup>, and again only 100 and 50 cm data were collected (10 and 14 diameters).

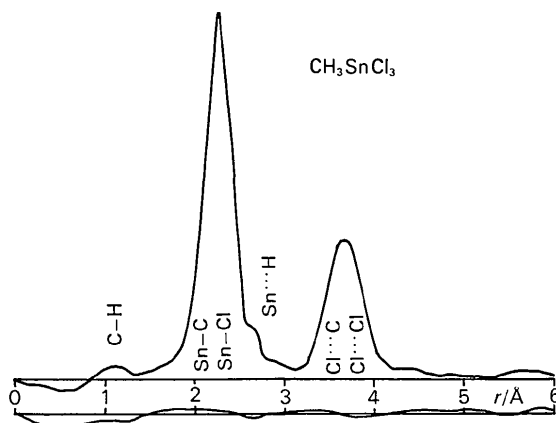


Fig. 1. Experimental radial distribution curve and difference curve for methyltrichlorostannane. (Damping constant, 0.004 Å<sup>2</sup>.)

*Dimethylstannane*

Preparation from dimethyldichlorostannane followed the method outlined for trimethylstannane, and diffraction patterns were recorded at  $-10^{\circ}\text{C}$ . The pat-

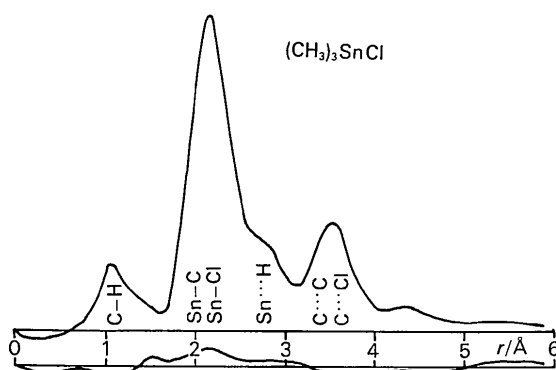


Fig. 2. Experimental radial distribution curve and difference curve for trimethylchlorostannane. (Damping constant,  $0.007 \text{ \AA}^2$ .)

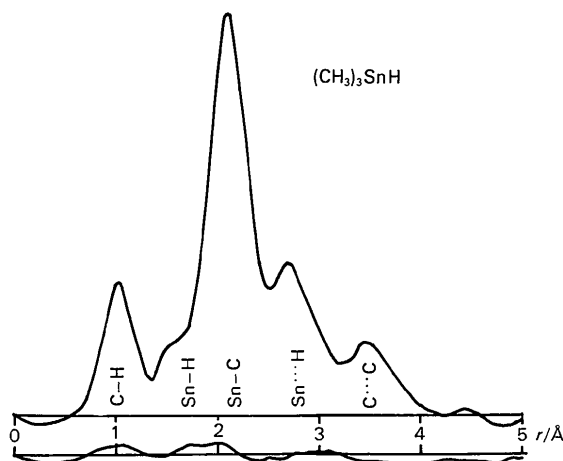


Fig. 3. Experimental radial distribution curve and difference curve for trimethylstannane. (Damping constant,  $0.006 \text{ \AA}^2$ .)

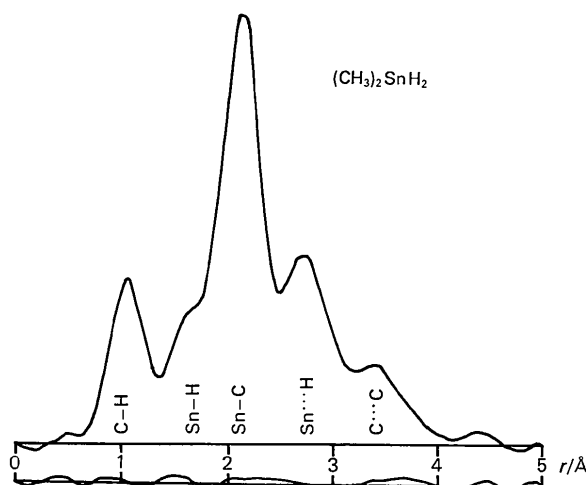


Fig. 4. Experimental radial distribution curve and difference curve for dimethylstannane. (Damping constant,  $0.005 \text{ \AA}^2$ .)

terns were very similar to those for trimethylstannane. The numbers of diameters scanned were 10 and 16 for the 100 and 50 cm camera distances, respectively.

**Structure determinations**

Intensity data were processed by routine methods (Beagley, Monaghan & Hewitt, 1971) and radial distribution (r.d.) curves for the four molecules were obtained (Figs. 1–4). Methyltrichlorostannane has the simplest r.d. curve (Fig. 1); it shows only two main peaks, in keeping with the tetrahedral geometry around tin. Bonds Sn–Cl and Sn–C are unresolved in the peak at about  $2 \text{ \AA}$ , and the peak at about  $3.6 \text{ \AA}$  is due to Cl...Cl and Cl...C; C–H is visible at  $\sim 1.1 \text{ \AA}$  and Sn...H weakly as a shoulder at  $\sim 2.6 \text{ \AA}$ . Assuming staggered C–H and Sn–Cl bonds, five parameters fix the  $C_{3v}$  geometry: Sn–Cl, Sn–C, C–H,  $\angle \text{ClSnCl}$  and  $\angle \text{SnCH}$ . As the r.d. curve has only two prominent peaks, only the two most strongly scattering distances, Sn–Cl and Cl...Cl, can be expected to be well determined, but these also allow accurate values for the angles at tin to be deduced.

In trimethylchlorostannane five independent parameters again fix  $C_{3v}$  geometry, but because there are now three methyl groups to one chlorine atom, the features attributable to distances involving the methyl groups are more prominent on the r.d. curve (Fig. 2). Again the peak at  $\sim 2 \text{ \AA}$  is due to Sn–Cl and Sn–C, but its Sn...H shoulder at  $\sim 2.7 \text{ \AA}$  is more pronounced than in Fig. 1. The C–H peak is also prominent. The peak at  $\sim 3.5 \text{ \AA}$ , which is due to C...C and Cl...C is not as prominent as in Fig. 1, as is to be expected. Some lack of resolution of Sn–Cl and Sn–C may still be expected, but the other independent parameters should be better determined than in methyltrichlorostannane. The peaks on the r.d. curve (Fig. 3) for  $C_{3v}$  trimethylstannane may be assigned as follows: C–H at  $1.1 \text{ \AA}$ , Sn–H at  $1.7 \text{ \AA}$  (shoulder), Sn–C at  $2.15 \text{ \AA}$ , Sn...H at  $2.75 \text{ \AA}$  and C...C at  $3.4 \text{ \AA}$ . Once again, there are five independent parameters (Sn–H, Sn–C, C–H,  $\angle \text{CSnC}$  and  $\angle \text{SnCH}$ ). In the absence of chlorine, the Sn–C distance is well determined because it is the sole contributor to its peak. However, poor resolution (as well as weak scattering) may be expected to limit the accuracy with which the Sn–H distance may be determined. In both the trimethyl compounds, the C–H bonds were assumed to be staggered with respect to the Sn–X bonds ( $X = \text{C}, \text{Cl}, \text{H}$ ).

The r.d. curve for dimethylstannane (Fig. 4) differs from that of trimethylstannane only by virtue of the different number of methyl groups involved. There are, however, six independent parameters; assuming  $C_{2v}$  symmetry and that the C–H and Sn–X bonds are mutually staggered, these are Sn–H, Sn–C, C–H,  $\angle \text{CSnC}$ ,  $\angle \text{SnCH}$  and  $\angle \text{HSnH}$ . With two Sn–H bonds present, Sn–H should be better determined than in trimethylstannane, but  $\angle \text{HSnH}$  and related  $\angle \text{HSnC}$  are poorly represented in the r.d. curve.

### Refinements and results

Full-matrix least-squares refinements of the structures of the four molecules were carried out on the basis of the molecular models described above. Diagonal weighting schemes were used, and refinements optimized agreement between observed and calculated molecular intensity curves (Beagley, Monaghan & Hewitt, 1971). As mentioned briefly by Beagley & McAloon (1971), preliminary results (especially for the vibrational amplitudes) depended crucially on the complex scattering factors employed, particularly for tin. Consequently, in the more comprehensive present work, parallel refinements have been carried out for each molecule using three sets of scattering factors: I, those of Cox & Bonham (1967); II, those obtained by

a calculation based on a Clementi (1963) Hartree-Fock atomic potential for H, C and Cl, and a Thomas-Fermi-Dirac potential for tin (Bonham & Strand, 1963); III, the approximate scattering amplitudes of Hanson, Herman, Lea & Skillman (1964), in conjunction with the analytical phases given by Bonham & Ukaji (1962) which are based on a Thomas-Fermi potential (Ibers & Hoerni, 1954). Our calculation of scattering factors II utilized the procedure of Peacher & Wills (1967). The results of the three refinements for each of the four molecules are given in Tables 1-4. To be consistent for a given molecule, only those parameters that converged in all three refinements could be varied. Finally, using scattering factors II, all the geometrical parameters for each molecule were refined, together with as many amplitudes as possible.

Table 1. *Methyltrichlorostannane, comparison of results obtained using various scattering factors\**

Parameters varied	I		II (this work)		III	
	Value	E.s.d.	Value	E.s.d.	Value	E.s.d.
Distances						
Sn—C	2.106 Å	0.022 Å	2.101 Å	0.018 Å	2.071 Å	0.022 Å
Sn—Cl	2.302	0.002	2.303	0.002	2.304	0.002
Cl···Cl	3.658	0.016	3.649	0.015	3.692	0.026
Sn···H	2.651	0.072	2.679	0.069	2.592	0.105
Amplitudes						
Sn—Cl	0.029	0.010	0.055	0.005	0.076	0.007
Cl···Cl	0.132	0.010	0.138	0.010	0.145	0.013

\* See text for details.

Table 2. *Trimethylchlorostannane, comparison of results obtained using various scattering factors\**

Parameters varied	I		II (this work)		III	
	Value	E.s.d.	Value	E.s.d.	Value	E.s.d.
Distances						
Sn—C	2.106 Å	0.005 Å	2.098 Å	0.004 Å	2.094 Å	0.004 Å
Sn—Cl	2.300	0.009	2.326	0.008	2.329	0.008
Sn···H	2.698	0.016	2.714	0.016	2.707	0.016
C···Cl	3.532	0.021	3.514	0.022	3.539	0.021
Amplitudes						
Sn···H	0.069	0.024	0.098	0.017	0.096	0.016
C···Cl	0.165	0.020	0.176	0.021	0.148	0.020

\* See text for details.

Table 3. *Trimethylstannane, comparison of results obtained using various scattering factors\**

Parameters varied	I		II (this work)		III	
	Value	E.s.d.	Value	E.s.d.	Value	E.s.d.
Distances						
Sn—C	2.147 Å	0.004 Å	2.148 Å	0.004 Å	2.147 Å	0.005 Å
Sn···H	2.734	0.013	2.743	0.012	2.708	0.015
C···C	3.455	0.024	3.459	0.022	3.426	0.022
Amplitudes						
Sn—C	0.015	0.027	0.075	0.009	0.083	0.011
Sn···H	0.105	0.018	0.140	0.013	0.142	0.020
C···C	0.124	0.030	0.128	0.028	0.105	0.030

\* See text for details.

Other amplitudes were fixed at reasonable values. The results of these final refinements are given in Table 5. In Tables 1–4, the estimated standard deviations quoted are derived from those given by the least-squares program and refer only to random uncertainties but are corrected for data correlation; those quoted in Table 5 also include systematic uncertainties.

### Discussion

The r.d. curves and their relatively featureless difference curves (Figs. 1–4) demonstrate that the general assumptions made about the four molecules are reasonable. Thus, methyltrichlorostannane, trimethylchlorostannane and trimethylstannane can reasonably be supposed to possess  $C_{3v}$  symmetry, and dimethyl-

stannane  $C_{2v}$ . If there are any deviations from these symmetries, they are due to rotations of methyl groups away from their staggered positions with respect to Sn–X bonds; the orientations of the methyl groups are poorly represented in the diffraction data. The r.d. curve for trimethylchlorostannane is probably the least satisfactory of the four. This may be attributed to the experimental difficulties encountered with this molecule; experimental difficulties are not, however, responsible for the disappearance of its diffraction rings at  $s \approx 16 \text{ \AA}^{-1}$ . All the molecules show this behaviour except methyltrichlorostannane, where  $s_{\max} \approx 26 \text{ \AA}^{-1}$ . The latter molecule is the only one of the four where Sn–Cl dominates the scattering, and the differing values of  $s_{\max}$  are readily attributable to the relative positions of the beat-out points in the diffraction patterns of

Table 4. *Dimethylstannane, comparison of results obtained using various scattering factors\**

Parameters varied	I		II (this work)		III	
	Value	E.s.d.	Value	E.s.d.	Value	E.s.d.
Distances						
Sn—C	2.151 Å	0.004 Å	2.151 Å	0.004 Å	2.153 Å	0.004 Å
Sn···H	2.733	0.012	2.738	0.010	2.732	0.011
Amplitudes						
Sn—C	–0.010	0.100	0.076	0.009	0.088	0.009
Sn···H	0.103	0.020	0.133	0.011	0.129	0.012

\* See text for details.

Table 5. *Final parameters\* of the four molecules, obtained using scattering factors II*

Parameter	Methyltrichlorostannane		Trimethylchlorostannane		Trimethylstannane		Dimethylstannane	
	Value	E.s.d.	Value	E.s.d.	Value	E.s.d.	Value	E.s.d.
Independent distances:								
Sn—C	2.104	0.016	2.106	0.006	2.147	0.004	2.150	0.003
Sn—Cl	2.304	0.003	2.351	0.007	—	—	—	—
Sn—H	—	—	—	—	1.705	0.067	1.680	0.015
C—H	1.100	fixed	1.125	0.015	1.086	0.010	1.080	0.007
C···C	—	—	3.550	†	3.462	0.011	3.407	0.010
C···Cl	3.696	†	3.497	0.008	—	—	—	—
Cl···Cl	3.648	0.009	—	—	—	—	—	—
Sn···H	2.651	0.050	2.754	0.013	2.740	0.007	2.740	0.005
C···H(Sn)	—	—	—	—	3.194	†	3.111	0.030
Amplitudes:								
Sn—C	0.056	fixed	0.061	0.024	0.071	0.009	0.085	0.007
Sn—Cl	0.055	0.005	0.089	0.020	—	—	—	—
Sn—H	—	—	—	—	0.110	fixed	0.098	0.015
C—H	0.080	fixed	0.136	0.020	0.063	0.020	0.062	0.016
C···C	—	—	0.120	fixed	0.119	0.013	0.127	0.018
C···Cl	0.147	0.010	0.168	0.009	—	—	—	—
Cl···Cl	0.138	0.007	—	—	—	—	—	—
Sn···H	0.227	0.060	0.123	0.013	0.143	0.008	0.121	0.005
Derived angles:								
∠CSnC	—	—	114.9	1.6	107.5	0.6	104.8	0.5
∠CSnCl	113.9	0.7	103.2	0.6	—	—	—	—
∠ClSnCl	104.7	0.4	—	—	—	—	—	—
∠CSnH	—	—	—	—	111.5	2.0	108.0	1.5
∠SnCH	107.5	2.0	113.4	1.4	111.6	0.7	111.7	0.5

\* Distances are  $r_g(1)$  values in Å. Amplitudes in Å. Angles in degrees. E.s.d.'s include a contribution for systematic errors.

† Dependent distance.

Sn-C and Sn-Cl. The beat-out points occur where the phase-sensitive  $\cos(\eta_i - \eta_j)$  term in the molecular intensity expression is zero; beat-out points occur at  $s \approx 16$  and  $s \approx 27 \text{ \AA}^{-1}$  for Sn-C and Sn-Cl respectively.

In the twelve refinements reported in Tables 1-4, the results of refinements using scattering factors II (those calculated by the present authors) are in general associated with lower e.s.d.'s (The lower e.s.d.'s occur because there is better agreement between observed and calculated intensities.) Again, trimethylchlorostannane does not quite fit into the general pattern; the e.s.d.'s for this molecule are more uniform between the refinements, probably because the uncertainties due to the poorer experimental data dominate the e.s.d.'s. For each of the four molecules, the vibrational amplitudes involving tin are invariably lower in refinements using scattering factors I; this is in agreement with the preliminary observations of Beagley & McAloon (1971), who attributed the low amplitudes to an error in the calculation of scattering factors I for tin. As scattering factors III are approximate, it is not surprising that they too give rise to slightly higher e.s.d.'s than do scattering factors II. The above discussion clearly indicates that the results obtained using scattering factors II are to be preferred, and subsequent discussion is based on the results of the extended refinements using them (Table 5).

The most striking feature of the results in Table 5 is the variability of the Sn-Cl and Sn-C bond lengths. When compared with similar bonds in other molecules, a clear pattern emerges (see Table 6, which reports  $r_g = r_g(0)$  distances). The Sn-Cl bonds decrease in length as methyl groups are successively replaced by chlorine atoms. This behaviour follows the general pattern observed in many systems (Beagley, 1973), that A-X bonds decrease in length as extra electronegative halogen atoms X are attached to atom A; for C-F bonds, calculations suggest that the decrease is associated with increased ionic character (Brown, 1971). The Sn-C bond lengths fall into two groups. Those where tin is also attached to chlorine lie in the narrow range 2.105-2.109 Å (weighted mean, 2.108 Å), and those where chlorine is absent lie in the range 2.134-

2.153 Å (mean 2.147 Å); once again the halogen has a shortening effect. Where chlorine is absent, there is some evidence that the Sn-C bond length decreases as methyl groups are added. The more electronegative group IV element in these methylstannanes is carbon, and the decrease in length as extra 'electronegative' methyl groups are added fits the general pattern noted above for bonds to halogens. Of the amplitudes given in Table 6, those for Sn-Cl show a slight trend that corresponds with the variation of the bond lengths: the shorter the bond, the smaller the amplitude. The Sn-C amplitudes, which are all of lower precision, have a weighted mean of 0.076 Å. All the calculated amplitudes for both Sn-Cl and Sn-C are lower than the corresponding observed values; this systematic difference may be due to the retention of a slight imperfection in the scattering factors, but anharmonic vibrations or an error in the harmonic force field are other possible sources of the disagreement.

The observed Sn-H bond lengths agree favourably with values found in other molecules (Lide, 1951; Wilkinson & Wilson, 1956).

Finally, it is noteworthy that in the solid phase, methylhalostannanes may not have the same structure as observed in the gas phase. In solid dimethyldichlorostannane, for example, adjacent molecules are linked by non-linear chlorine bridges (Sn-Cl=2.40, 3.54 Å), giving rise to a very distorted octahedral tin coordination (Davies, Milledge, Puxley & Smith, 1970); in trimethylfluorostannane, the tin atom is probably in fivefold coordination, because of fluorine bridging (Clark, O'Brien & Trotter, 1964).

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Table 6.  $r_g$  Bond lengths and amplitudes in Å for some tin compounds

Molecule	Sn-C		Sn-Cl		Reference
	Distance	Amplitude†	Distance	Amplitude†	
MeSnH <sub>3</sub>	2.150* ± 0.005	-	-	-	Lide (1951)
Me <sub>2</sub> SnH <sub>2</sub>	2.153 ± 0.004	0.085 ± 0.007	-	-	This work
Me <sub>3</sub> SnH	2.149 ± 0.004	0.071 ± 0.009	-	-	This work
Me <sub>4</sub> Sn	2.134 ± 0.003	-	-	-	Preliminary result, see Fujii & Kimura (1971)
Me <sub>3</sub> SnCl	2.108 ± 0.006	0.061 ± 0.024	2.354 ± 0.008	0.089 ± 0.020	This work
Me <sub>2</sub> SnCl <sub>2</sub>	2.109 ± 0.003	0.075 ± 0.008 (0.054)	2.327 ± 0.002	0.061 ± 0.003 (0.054)	Fujii & Kimura (1971)
MeSnCl <sub>3</sub>	2.105 ± 0.016	0.056, fixed	2.306 ± 0.003	0.055 ± 0.005	This work
SnCl <sub>4</sub>	-	-	2.281 ± 0.002	0.050 ± 0.003 (0.046)	Fujii & Kimura (1970)

\*  $r_g$  Value estimated from microwave, partial  $r_0$ , value of 2.143 ± 0.002 Å.

† In parentheses are values calculated from spectroscopic data (see references for details).

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## The Conformation of Non-Aromatic Ring Compounds. LXXXII.\* The Crystal and Molecular Structure of *cis, trans*-2,5-Di-*t*-butylcyclohexanol Toluene-*p*-sulphonate

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The structure has been determined from three-dimensional X-ray data. The crystals are monoclinic, space group  $P2_1/n$  with  $Z=4$ . The unit-cell dimensions are  $a=12.562$ ,  $b=28.402$ ,  $c=5.964$  Å and  $\beta=94.9^\circ$ . The final conventional  $R$  value is 4.2%. The cyclohexane ring has a chair conformation with the two *t*-butyl groups in equatorial position. The *t*-butyl groups are twisted away from the staggered form by about  $-12$  and  $+7^\circ$  respectively. The thermal motion has been analysed in terms of a rigid body, and suggests a fairly large torsional motion of the *t*-butyl groups.

### Introduction

The presence of *t*-butyl groups in cyclohexane-like molecules introduces a considerable amount of 'strain', perhaps mainly due to short intramolecular contacts between the hydrogen atoms of the *t*-butyl group and the nearest hydrogens of the rest of the molecule. In the case of *t*-butylcyclohexane and related molecular systems this strain is partly relieved by an extra flattening of the ring in the C(3)–C(4)–C(5) region as well as by an increase of the exocyclic C–C–C bond angles to about  $114^\circ$ . Empirical force-field calculations (Altona & Sundaralingam, 1970) led to the prediction that in the minimum energy conformation of *t*-butylcyclohexane the *t*-butyl group does not occupy a staggered position, but is twisted ( $\pm 17^\circ$ ) with respect to the ring bonds, accompanied by an asymmetric distortion of the ring itself. Since the barrier separating the two equivalent forms was calculated to be only 0.2–

0.3 kcal mole<sup>-1</sup>, an X-ray analysis would show a time-average picture, *i.e.* staggering of the *t*-butyl group accompanied by large temperature factors of its methyl carbon atoms. Asymmetric substitution, causing sufficiently strong steric interference, will render the two forms non-equivalent and this would result in a time-average twist different from zero. Further theoretical work threw some doubt on the existence of a double minimum potential energy well – it might result from deficiencies in the force field employed (Altona & Faber, 1973) – but a potential energy well with a wide 'flat' minimum would still lead to the same predictions.

A number of X-ray studies on symmetrically substituted 4-*t*-butylcyclohexanes and related compounds has since appeared in which the off-staggering of the *t*-butyl group did not exceed  $3^\circ$  (Cook, Glick, Rigau & Johnson, 1971; Berti, Macchia, Macchia, Merlino & Muccini, 1971; Lectard, Metras, Petrisans & Gaultier, 1971; Parthasarathy, Ohrt, Kagan & Fiaud, 1972; Johnson, Cheer, Schaefer, James & Moore, 1972; Johnson, Schaefer, James & McConnell, 1972; de

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