Conformational Studies of Dicyclohexylthallium Chloride, Bis(4-methylcyclohexyl)thallium Chloride and Bis(4-*tert*-butylcyclohexyl)thallium Chloride by ^{1}H NMR

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Vicinal thallium–hydrogen coupling constants are used to discuss conformations in dicyclohexylthallium chloride, bis(4-methylcyclohexyl)thallium chloride and bis(4-*tert*-butylcyclohexyl)thallium chloride. Thallium does not have a very strong preference for equatorial positions in dicyclohexylthallium chloride, whereas bis(4-alkylcyclohexyl)thallium chlorides exist largely in one conformation. Bis(4-methylcyclohexyl)thallium chloride exists in three isomeric forms; the major product appears to be the *cis*-isomer (equatorial methyl, axial thallium), with the other two isomers probably containing thallium *trans* to the methyl group (axial thallium being preferred). The preference for the *cis*-isomer (equatorial *tert*-butyl, axial thallium) of bis(4-*tert*-butylcyclohexyl)thallium chloride is such that other isomers are not obtained.

INTRODUCTION

In monosubstituted cyclohexanes the equatorial–axial equilibria have been frequently studied and *A* values (ΔG° in kcal mol^{-1} for the equatorial-to-axial conformational change) have been tabulated for many groups.[1] A marked equatorial preference is found for nearly all substituents examined,[1,2] and it was assumed until recently that metal-containing groups followed this pattern, because of their large atomic radii. 1,3-Diaxial interactions, however, would be expected to be reduced by longer carbon—metal bonds. It was thus of importance when Jensen and Gale[3] reported that the benzoxymercuric group, compared with methyl, had a relatively small conformational preference, and low *A* values (*ca* 0.0) were subsequently reported by Jensen *et al.*[2] for the bromomercuric[4] and acetoxymercuric groups. Anet *et al.*[5] re-investigated the conformational equilibria of cyclohexylmercuric compounds by high-field ^{1}H and ^{13}C NMR, and demonstrated that —HgOAc and —HgCl can have distinctly negative A values; this was the first example of a monosubstituted cyclohexane preferring the axial form.

A more detailed study of the cyclohexylmercury system[6] confirmed that the axial conformer is preferred for a wide range of cyclohexylmercuric compounds, and for dicyclohexylmercury (CD_2Cl_2–pyridine-d_5 solvent) at 193 K three species (a,a; e,a; a,e) were detected by ^{13}C NMR, with the (*a,a*) conformer being most favoured. In our study the conformational equilibria in bis(cyclohexyl)thallium compounds and, *inter alia*, the observation of a dihedral angle dependence of the vicinal ^{205}Tl–^{1}H coupling is reported.

RESULTS AND DISCUSSION

Dicyclohexylthallium chloride

Both 60 and 90 MHz ^{1}H NMR spectra were obtained and assigned as described elsewhere.[7] The width of individual peaks ($W/2 \approx 30$ Hz) can be attributed to the many spin–spin couplings involved (i.e. ^{203}Tl–H, ^{205}Tl–H, H–H couplings in the cyclohexane ring). The large width of the peaks in the ^{1}H NMR spectrum of a D_2O solution of dicyclopentylthallium sulphate was attributed by Maher and Evans[8] to molecular motion in the cyclopentane ring, although this explanation seems doubtful for dicyclohexylthallium chloride as there is no apparent variation in line width at half-height with temperature. Results for dicyclohexylthallium chloride are summarized in Table 1. Variable-temperature spectra (with pyridine-d_5 as solvent) demonstrate that both vicinal thallium–hydrogen couplings increase, although not to the same extent, with an increase in temperature. These temperature and solvent dependences could arise from differences in (a) conformational equilibrium [angular variation of $J(\mathrm{Tl, H})$], (b) degrees of ionization, $R_2TlCl \rightleftharpoons R_2Tl^+ + Cl^-$, and (c) degree of complex formation between solvent and solute.

Bis(4-alkylcyclohexyl)thallium chlorides, discussed later, give further information on these variations, and the results suggest that (a) above is the important factor for dicyclohexylthallium chloride, where it is reasonable to interpret the results in terms of a con-

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Table 1. Tl–H coupling constants for solutions of dicyclohexylthallium chloride

Temperature (°C)	$^3J(\text{Tl}, \text{H}_M)$[a] (Hz)	$^2J(\text{Tl}, \text{H}_G)$ (Hz)	$^3J(\text{Tl}, \text{H}_N)$ (Hz)
23	518(D)[b]	369(D)	213(D)
23	502(P)[b]	329(P)[c]	213(P)[c]
88	563(P)	328(P)[c]	221(P)[c]
100	575(P)		224(P)[c]

[a] See Fig. 1 for hydrogen notation.
[b] Solvent: P = C_5D_5N; D = $(CD_3)_2SO$.
[c] Measurements made on overlapping peaks.

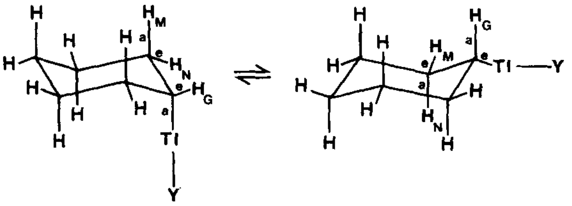

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Figure 1. Chair conformations of dicyclohexylthallium chloride. For simplification, the second cyclohexyl group is depicted as Y and the chlorine atom has been omitted.

formational equilibrium (Fig. 1). For this equilibrium the observed value of $^3J(\text{Tl}, \text{H}_M)$ (502 Hz) is a weighted average of $J[\text{Tl(a)}, \text{H(a)}]$ and $J[(\text{Tl(e)}, \text{H(e)}]$ (a and e indicating axial and equatorial orientations), while the observed value of $^3J(\text{Tl}, \text{H}_N)$ (213 Hz) is a weighted average of $J[\text{Tl(e)}, \text{H(a)}]$ and $J[\text{Tl(a)}, \text{H(e)}]$. $^2J(\text{Tl}, \text{H}_G)$ (329 Hz) would be expected to be almost independent of conformational changes. It was assumed that the largest thallium–hydrogen coupling is $J[\text{Tl(a)}, \text{H(a)}]$, and that, as a result of 1,3-diaxial interactions in dicyclohexylthallium chloride, thallium will prefer to adopt an equatorial position. Thus the effect of raising the temperature is to increase the proportion of conformer having an axial thallium, with the subsequent observed increase in $J(\text{Tl}, \text{H}_M)$. On the basis of this increase it would appear that thallium does not have a very strong conformational preference.

Bis(4-alkylcyclohexyl)thallium chlorides

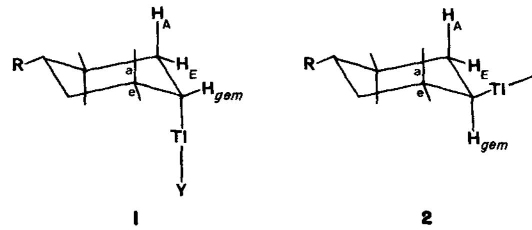
Unpurified samples of bis(4-*tert*-butylcyclohexyl)-thallium chloride gave satisfactory ^{1}H NMR spectra, but poor yields and the failure to obtain an analytical sample led to studies of bis(4-methylcyclohexyl)-thallium chloride. The synthesis of this compound from mixed isomers of 4-methylcyclohexyl chloride gave a material (A) (from pyridine extraction) that gave a satisfactory analysis and which, from its ^{1}H NMR spectrum, appeared to be a single isomer. Since yields of the compound were low, the diethyl ether layer, which is normally rejected in syntheses of dialkylthallium chlorides, was examined. This yielded material which appeared from ^{1}H NMR to be a mixture of two isomers, A and B. Synthesis of bis(4-methylcyclohexyl)thallium chloride from *cis*-4-methylcyclohexyl chloride produced isomer A (from both pyridine and diethyl ether extracts) whilst *trans*-4-methylcyclohexyl chloride yielded isomer A (from the pyridine extract) and isomers A, B and C (from the diethyl ether extract). It was found impossible to separate these three isomers by differential solubility in organic solvents and, thus, not advantageous to separate the *cis* and *trans* isomers of the alkyl halide. ^{1}H NMR spectra (60 and 90 MHz) were obtained for bis-(4-alkylcyclohexyl)thallium chlorides and results are summarized in Table 2.

Table 2. Tl–H coupling constants for solutions of bis(4-alkylcyclohexyl)thallium chloride at 23 °C

Compound	Isomer	$^2J(\text{Tl}, \text{H})$ (Hz)	$^3J(\text{Tl}, \text{H})$ (Hz)
$(4\text{–}CH_3C_6H_{10})_2TlCl$	A[a]	438[b](C)[c]	1153(C) 1055(P)[c] 1055(P) (88 °C)
	A[d]		1162(C)
	A[e]		1144(C)
	B, C[e]		980, 1050 or 1010, 1020[f](C)
	A[g]		1168(C)
$(4\text{-}tert\text{-}C_4H_9C_6H_{10})_2TlCl$	A[a]	454[b](C)	1182(C) 1179(P)

[a] From mixed isomers of the alkyl halide.
[b] From 60 and 90 MHz spectra.
[c] Solvent: C = $CDCl_3$; P = C_5D_5N.
[d] Pyridine extract of organothallium compound from *trans*-alkyl halide.
[e] Ether extract of organothallium compound from *trans*-alkyl halide.
[f] Two doublets not present in the spectrum of isomer A; one peak partly obscured. Pairing of doublet components uncertain.
[g] Ether and pyridine extracts of organothallium compound from *cis*-alkyl halide.

Further structural information can be obtained by extending line width criteria proposed by Lemieux *et al.*[9] for *cis*- and *trans*-4-*tert*-butylcyclohexyl alcohols and acetates to bis(4-alkylcyclohexyl)thallium chlorides. Possible configurations for the latter are shown in **1** and **2**, using the assumption that the alkyl group preferentially adopts an equatorial position. Using typical values for $J(\text{H}, \text{H})$ in cyclohexyl compounds[10] ($J_{aa} \approx J_{gem} \approx 12$ Hz, $J_{ae} \approx 5$ Hz and $J_{ee} \approx 3$ Hz) and making an allowance for the difference between $J(^{203}\text{Tl}, \text{H})$ and $J(^{205}\text{Tl}, \text{H})$, it is possible to estimate[7] approximate line widths for H_A, H_E and H_{gem} resonances in bis(4-alkylcyclohexyl)thallium chlorides. Comparison of the estimated (for the two configurations) and observed ratios of line widths relative to



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The second alkylcyclohexyl group is depicted as Y, R denotes an alkyl group and the chlorine atom has been omitted.

that for H_{gem} in isomer A indicates that (a) the geminal hydrogen is equatorial (**1**) and (b) the large coupling is $J(\mathrm{Tl}, H_A)$, and involves an axial–axial spin–spin coupling (**1**).

The observed quarter-height line width of the H_{gem} peak (18–20 Hz) also indicates that this hydrogen atom occupies the equatorial position in structure **1**. Peak-height measurements on the ^{1}H NMR spectrum of bis(4-*tert*-butylcyclohexyl)thallium chloride enable the same conclusions to be drawn as for isomer A of bis(4-methylcyclohexyl)thallium chloride. Isomers B and C show slightly smaller values of $^3J(\mathrm{Tl}, \mathrm{H})$ than isomer A, whereas for bis(4-*tert*-butylcyclohexyl)thallium chloride in chloroform-*d* the vicinal coupling was slightly larger than that for isomer A, and there were no indications of a second or third isomer.

There is no variation of the large $^3J(\mathrm{Tl}, \mathrm{H})$ coupling with temperature for bis(4-methylcyclohexyl)thallium chloride and this observation, together with the magnitude of the coupling, suggests isomer A is largely in one conformation (**1**). This also provides evidence that, for a given solvent, variations in $^3J(\mathrm{Tl}, \mathrm{H})$ with temperature for dicyclohexylthallium chloride are due to a conformational equilibrium, and not from differences in either the degrees of ionization or complex formation between solvent and solute. At room temperature using different solvents, chloroform-*d* and pyridine-d_5, $^3J(\mathrm{Tl}, \mathrm{H})$ in bis(4-methylcyclohexyl)thallium chloride is different; this may be a result of changes in degree of ionization or complex formation. Since chloroform has a lower dielectric constant (ε = 4.806 at 20 °C)[11] than pyridine (ε = 12.3 at 25 °C),[11] a smaller degree of ionization is indicated in chloroform, consequently suggesting that the smaller couplings observed for pyridine solutions are due to complex formation.

There is no evidence for the configuration (*cis* or *trans*) of bis(4-methylcyclohexyl)thallium chloride as a whole. It is probable that A, the major isomer, is *cis* (**3**), with the methyl group in the conformationally preferred equatorial position. For the B and C isomers the large $^3J(\mathrm{Tl}, \mathrm{H})$ coupling would, on the basis of the present hypothesis, require an axial thallium, necessitating an axial methyl group (**4**); this point is discussed later.

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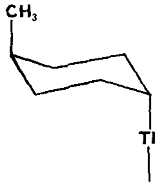

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The second alkylcyclohexyl group and the chlorine atom have been omitted.

Equilibrium calculations for dicyclohexylthallium chloride

Using results and conclusions for bis(4-alkylcyclohexyl)thallium chlorides, the results for dicyclohexylthallium chloride can be considered further. The thallium–hydrogen couplings for a molar fraction x of conformer I and $1-x$ of conformer II (see Fig. 1) for dicyclohexylthallium chloride can be calculated using Eqns (1) and (2) and x can be determined by rearrangement

$$J(\mathrm{Tl}, H_M) = xJ[\mathrm{Tl(a)}, \mathrm{H(a)}] + (1-x)J[\mathrm{Tl(e)}, \mathrm{H(e)}] \quad (1)$$

$$J(\mathrm{Tl}, H_N) = xJ[\mathrm{Tl(a)}, \mathrm{H(e)}] + (1-x)J[\mathrm{Tl(e)}, \mathrm{H(a)}] \quad (2)$$

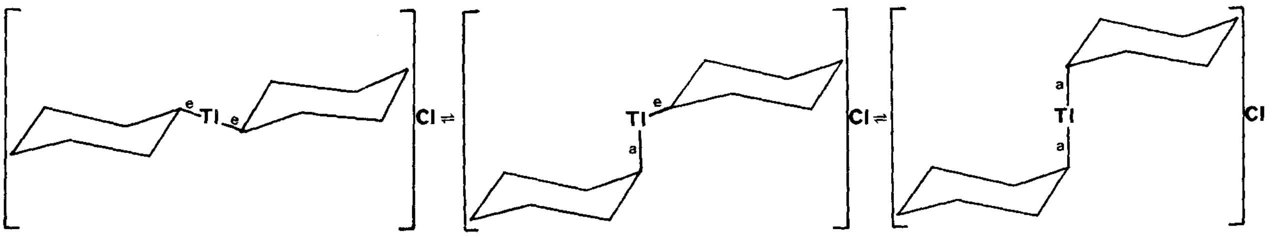
of either equation. The preparation of bis(4-methylcyclohexyl)thallium chloride from separate isomers of 4-methylcyclohexyl chloride did not provide further information on $J[\mathrm{Tl(a)}, \mathrm{H(a)}]$, $J[\mathrm{Tl(a)}, \mathrm{H(e)}]$, $J[\mathrm{Tl(e)}, \mathrm{H(a)}]$ and $J[\mathrm{Tl(e)}, \mathrm{H(e)}]$. Values of $J[\mathrm{Tl(a)}, \mathrm{H(a)}]$ [from bis(4-alkylcyclohexyl)thallium chlorides] and $J[\mathrm{Tl(a)}, \mathrm{H(e)}]$ (from dicyclohexylthallium chloride), but not $J[\mathrm{Tl(e)}, \mathrm{H(e)}]$, were obtained and in the absence of an experimentally determined value for the latter, the observed value of $J[\mathrm{Tl(a)}, \mathrm{H(e)}]$ was used as a guide. Assuming that $J(\mathrm{Tl}, \mathrm{H})$ and $J(\mathrm{H}, \mathrm{H})$ show similar angular dependences, $J[\mathrm{Tl(a)}, \mathrm{H(e)}]$, 213 Hz, would be slightly larger than $J[\mathrm{Tl(e)}, \mathrm{H(e)}]$, and in subsequent calculations the molar fraction, x, was calculated using Eqn (1) for a number of possible values of $J[\mathrm{Tl(e)}, \mathrm{H(e)}]$ over the range 123–268 Hz using the value of $J[\mathrm{Tl(a)}, \mathrm{H(a)}]$ from bis(4-*tert*-butylcyclohexyl)thallium chloride.

These calculations indicated that thallium does not have a strong preference for an equatorial position and the equilibria $\mathbf{5} \rightleftharpoons \mathbf{6} \rightleftharpoons \mathbf{7}$ exist. Thallium–hydrogen coupling constants give values of relative numbers of *rings* with equatorial and axial thallium, but do not directly provide information about relative numbers of **5**, **6** and **7**; this is given via an equilibrium constant, K, which was calculated assuming the free energy changes involved in the conformational transitions ee → ea and ea → aa are equivalent. These calculations are detailed elsewhere.[7] Values of x, K, ΔG and the molar fractions of conformers **5**, **6** and **7** are presented in Table 3. The sign of the free energy changes indicates that the driving tendency of the equilibria is from right to left, and supports the assumption that in dicyclohexylthallium chloride, thallium has a small difference for equatorial positions. Calculation of the molar fraction, x, at 100 °C [where $J(\mathrm{Tl}, H_M) = 575$ Hz] using $J[\mathrm{Tl(e)}, \mathrm{H(e)}] = 213$ Hz, yields 0.38 compared with 0.30 (at room temperature).

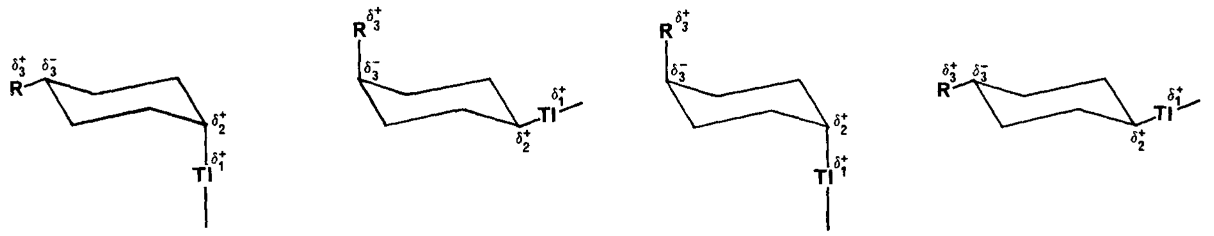
Although a wide range of $J[\mathrm{Tl(e)}, \mathrm{H(e)}]$ values were used in the calculations, the resultant ranges of x

Table 3. Equilibrium calculations for dicyclohexylthallium chloride

$J[\mathrm{Tl(e)}, \mathrm{H(e)}]$ (Hz)	x	K	ΔG (kcal mol^{-1})	(aa) **7**	(ea) **6**	(ee) **5**
123	0.36	0.65	0.26	0.20	0.32	0.50
141	0.35	0.63	0.27	0.20	0.30	0.48
159	0.34	0.61	0.29	0.20	0.30	0.50
177	0.32	0.57	0.34	0.18	0.30	0.50
195	0.31	0.55	0.36	0.16	0.30	0.54
213	0.30	0.53	0.38	0.16	0.30	0.56
231	0.29	0.51	0.40	0.16	0.28	0.56
249	0.27	0.47	0.44	0.14	0.28	0.60
268	0.26	0.45	0.47	0.12	0.28	0.62



(ee) **5** (ae) **6** (aa) **7**



8 **9** **10** **11**

R denotes an alkyl group and both the chlorine atom and second alkylcyclohexyl group have been omitted.

(0.26–0.36) and ΔG (0.26–0.47 kcal mol^{-1}) are relatively narrow. An exact value for J[Tl(e), H(e)] was impossible to determine experimentally, but the results indicate that thallium has a small conformational preference for equatorial positions in dicyclohexylthallium chloride. If $x = 0.1$ (corresponding to $\Delta G = 1.28$ kcal mol^{-1}) is substituted in Eqn (1), the resulting J[Tl(e), H(e)] is 427 Hz, indicating that if thallium had a large conformational preference for equatorial positions the magnitude of J[Tl(e), H(e)] would be approximately twice the value used. There is no evidence that J[Tl(e), H(e)] is likely to be of this magnitude.

Further consideration of the isomers of bis(4-methylcyclohexyl)thallium chloride

As the thallium atom in dicyclohexylthallium chloride has a preference for between 0.3 to 0.5 kcal mol^{-1} (over the range J[Tl(e), H(e)] = 123–268 Hz) for the equatorial position, the configurations of bis(4-methylcyclohexyl)thallium chloride must be considered, the methyl group having an equatorial preference (1.4–1.9 kcal mol^{-1}).[10] Evidence is increasing for attractive electronic interactions between polar substituents associated with six-membered rings. In 1,4-*trans*-substituted cyclohexane derivatives there are marked deviations[12] from the expected behaviour when the substituents are polar atoms or groups (X = Cl, Br or CF_3COO). This phenomenon is explained on the basis that polarization of the C—X bonds results in partial charges, with the concomitant attractive interaction between C-1 and X-4 (X bonded to C-4), and between C-4 and X-1 (X bonded to C-1), being larger in the di-axial than in the di-equatorial conformation, as the internuclear distance separating C-4 and X-1 is smaller in the di-axial conformation. In addition, the fact that the X–X distance is greater than the C–X distance means that X–X repulsions will be outweighed by the attractive interactions. In similar situations other transannular substituent effects have been observed.[13]

The ion R_2Tl^+ is suggested to exist in polar solvents from the conductivities of the sparingly soluble halides, R_2TlX (R = methyl, ethyl, *n*-propyl or *n*-butyl).[14,15] Although no conductivity data are available for dicyclohexylthallium chloride, the chloride has been exchanged for anions such as iodide,[16] nitrate[17,18] and carbonate,[18] and the dicyclohexylthallium(III) ion used as a reagent for the gravimetric and volumetric determination of nitrate.[18] Hence it is reasonable to assume that bis(4-alkylcyclohexyl)thallium chlorides in solution are probably ionized to some extent, so that the thallium atom carries a net positive charge (δ_1^+) which, in turn, will induce a small positive charge at C-1 (δ_2^+); the alkyl group will by inductive interaction be slightly positive (δ_3^+), whilst C-4 will be slightly negative (δ_3^-) (Fig. 2). As δ_2 and δ_3 are probably smaller than δ_1, it is possible that the most important polar interactions are those of an electrostatic nature involving thallium. For the *cis*-configuration, the possible conformers **8** and **9** are such that in **8** the normal R preference (*ca* 1.5–1.9 kcal mol^{-1} for R = CH_3)[10] and the thallium polar

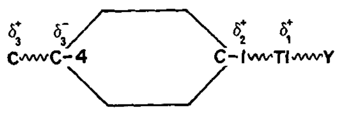


Figure 2. Charge distributions for bis(4-alkylcyclohexyl)thallium chlorides in solutions. For clarity, the second alkylcyclohexyl group is depicted as Y and both the chlorine atom and hydrogen atoms in the alkyl group have been omitted.

preference are satisfied whilst the normal (*ca* 0.4 kcal mol^{-1}) thallium preference is not; the converse holds for **9**. It would seem that **8** is the preferred conformation for this configuration. In the *trans*-configuration the possible conformers are **10** and **11**. The thallium polar requirements, but not the normal R and normal thallium interactions, are satisfied by **10**, whilst the converse applies to **11**. This configuration would seem a more likely candidate to be less conformationally biased than the *cis*-isomer.

As a working hypothesis it is reasonable to assume that isomer A of bis(4-methylcyclohexyl)thallium chloride (the major product) is the *cis*-isomer and that isomers B and C contain thallium *trans* to the methyl group (axial thallium being preferred), with the smaller values of J(Tl, H) being due to conformational equilibrium. The difference between B and C could be that in one isomer thallium is *trans* to the methyl group in both rings, whilst in the other isomer a mixture of *cis* and *trans* configurations exists. For bis(4-*tert*-butylcyclohexyl)thallium chloride the preference for the *cis*-isomer in conformation **8** is so great, owing to the bulky *tert*-butyl group, that other isomers are not obtained.

As the ion R_2Tl^+ is isoelectronic with R_2Hg, the corresponding mercury compound, and there are similarities between organo-mercury and -thallium compounds, it is likely that angular dependences of ^3J(Hg, H)[19] and ^3J(Tl, H) would be similar. 4-Methylcyclohexylmercuric compounds were thus studied for the purpose of observing differences between J(Hg, H) in the *cis*- and *trans*-isomers and comparing magnitudes with J(Tl, H) in the analogous organothallium compounds. Further, if values of vicinal mercury–hydrogen coupling constants could be obtained for axial–axial, axial–equatorial and equatorial–equatorial dispositions of coupled nuclei, ratios of coupling constants could be used to estimate ^3J[Tl(e), H(e)]. Unfortunately, for most Hg–H couplings only half of the ^{199}Hg satellites were detectable, companion satellites being obscured by other ring hydrogen resonances, so this study was of limited help.

Comparing thallium and mercury, both elements show angular dependences of their vicinal coupling constants, the largest values occurring for a dihedral angle of approximately 180°. Thallium shows only a small conformational preference for equatorial positions in dicyclohexylthallium chloride, whereas bis(4-alkylcyclohexyl)thallium chlorides exist largely in one conformation.

EXPERIMENTAL

^{1}H NMR spectra (measured in pyridine-d_5, dimethyl sulphoxide-d_6 or chloroform-d solution) were obtained on a JEOL C-60-H spectrometer operating at 60 MHz, using 5 mm spinning samples. Spectra were recorded in the field-sweep mode with the field-frequency stabilization circuitry activated by the signal from an external water sample. The concentrations of the samples were 0.07–0.3 M.

4-Methylcyclohexyl chloride (mixed *cis*- and *trans*-isomers)

A 0.876 mol amount of commercial 4-methylcyclohexanol (*trans*-rich), 203 ml of concentrated hydrochloric acid and 1.65 mol of anhydrous zinc chloride were refluxed with stirring, under nitrogen, for 3 h. The dark green upper organic layer was separated and dissolved in diethyl ether whilst the pale yellow aqueous layer was diluted with water and extracted with diethyl ether. The combined organic extracts were washed with water, dried (Na_2SO_4) and stripped. Distillation of the residual liquid yielded a small forerun of methylcyclohexenes, b.p. 19 °C/30 Torr (lit.,[20,21] 103 °C/760 Torr for 4-methylcyclohexene) and a mixture of *cis*- and *trans*-4-methylcyclohexyl chlorides in 56% yield, b.p. 48–50 °C/20 Torr (lit.,[22] 40 °C/10 Torr), with the *trans*-isomer being predominant, as established by ^{1}H NMR[23] and IR.[24]

cis-4-Methylcyclohexyl chloride

The synthesis was based on the method of Lee and Downie[25] for the conversion of hydroxyesters to chloroesters. A 0.3 mol amount of commercial 4-methylcyclohexanol (*trans*-rich), 0.33 mol of dry triphenylphosphine and 600 ml of anhydrous carbon tetrachloride were stirred under reflux, whilst protected from moisture, for 9 h. After cooling, 600 ml of pentane were added to precipitate the bulk of the triphenylphosphine oxide. The mixture was filtered and the filtrate dried (Na_2SO_4) and stripped. Distillation of the residual liquid yielded a small forerun of methylcyclohexenes, b.p. 19 °C/30 Torr (lit.,[20,21] 103 °C/760 Torr for 4-methylcyclohexene) and *cis*-4-methylcyclohexyl chloride in 41% yield, b.p. 48–50 °C/20 Torr (lit.,[26] 41 °C/10 Torr).

trans-4-Methylcyclohexyl chloride

This was prepared in 21% yield by treatment of 4-methylcyclohexyl chloride (mixed *cis*- and *trans*-isomers) with potassium hydroxide by the procedure of Greene *et al.*[27]

4-*tert*-Butylcyclohexyl chloride (mixed *cis*- and *trans*-isomers)

This synthesis used commercial 4-*tert*-butylcyclohexanol (*trans*-rich), and was similar to that for 4-methylcyclohexyl chloride (mixed *cis*- and *trans*-isomers) up to and including evaporation of the diethyl ether. The following description deals with processes after that stage. Distillation of the residual liquid yielded a small forerun of *tert*-butylcyclohexenes, b.p. 57–65 °C/14 Torr (lit.,[28] 65 °C/14 Torr for 4-*tert*-butylcyclohexene) and a mixture of *cis*- and *trans*-4-*tert*-butylcyclohexyl chlorides in 49% yield, b.p. 100–102 °C/20 Torr (lit.,[29] 127 °C/52 Torr), with the *trans*-isomer being predominant, as established by ^{1}H NMR[29] and IR.[29,30]

Dicyclohexylthallium chloride

This synthesis was based on the method of Krause and von Grosse,[17] which is complicated by the concomitant formation of oxidation products of the Grignard reagent by thallium(III) chloride. A 0.07 mol amount of ethereal thallium(III) chloride was added dropwise, under nitrogen, to a continuously stirred solution of 0.186 mol of ethereal cyclohexylmagnesium chloride at −15 °C (ice–sodium chloride bath). Following the addition the stirred reaction mixture was allowed to warm slowly to room temperature and stirred for a further 30 min. The reaction mixture was hydrolysed at −15 °C by the slow addition, whilst stirring, of dilute HCl and filtered. The collected solids were extracted with boiling pyridine and filtered to remove metallic thallium and thallium(I) chloride. The filtrate yielded dicyclohexylthallium chloride, which was recrystallized from aqueous pyridine.

Analysis: calculated for $C_{12}H_{22}TlCl$, C 35.49, H 5.46, Cl 8.73, Tl 50.32; found, C 35.5, H 5.33, Cl 8.79, Tl 50.08%.

Bis(4-Alkylcyclohexyl)thallium chlorides

The syntheses were similar to that for dicyclohexylthallium chloride, up to and including hydrolysis with dilute HCl. Thus the following procedures deal only with processes after that stage. Organothallium compounds from diethyl ether and pyridine extracts were recrystallized from aqueous pyridine.

Bis(4-methylcyclohexyl)thallium chloride (from mixed isomers of 4-methylcyclohexyl chloride). The collected grey solids (from filtration of the hydrolysed reaction mixture) were washed with diethyl ether, extracted with pyridine and filtered. Concentration of the filtrate yielded bis(4-methylcyclohexyl)thallium chloride (isomer A). The aqueous layer (from hydrolysis with dilute HCl) was extracted twice with diethyl ether. The combined diethyl ether extracts were washed with water, dried (Na_2SO_4) and stripped to yield bis(4-methylcyclohexyl)thallium chloride (isomers A and B) and a viscous liquid (possibly isomeric 4,4′-dimethylbicyclohexyls formed by a Wurtz-type side reaction), which was removed by evaporation under vacuum.

Analysis: calculated for $C_{14}H_{26}TlCl$, C 38.73, H 6.04, Cl 8.16, Tl 47.07; found (isomer A), C 38.88, H 5.96, Cl 7.54, Tl 47.8%.

Bis(4-methylcyclohexyl)thallium chloride (from *trans*-4-methylcyclohexyl chloride). A pyridine extraction of the grey solid (from filtration of the hydrolysed reaction mixture) yielded bis(4-methylcyclohexyl)thallium chloride (isomer A) and a diethyl ether extraction yielded bis(4-methylcyclohexyl)thallium chloride (isomers A, B and C).

Bis(4-methylcyclohexyl)thallium chloride (from *cis*-4-methylcyclohexyl chloride). Both pyridine and diethyl ether extracts yielded bis(4-methylcyclohexyl)thallium chloride (isomer A).

Bis(4-*tert*-butylcyclohexyl)thallium chloride (from mixed isomers of 4-*tert*-butylcyclohexyl chloride). A pyridine extraction of the grey solid yielded material devoid of any organothallium compound. Treatment of the diethyl ether layer yielded a liquid containing bis(4-*tert*-butylcyclohexyl)thallium chloride (isomer A) and a large amount of 4,4′-di-*tert*-butylbicyclohexyls (formed by Wurtz-type side reaction), most of which was removed by evaporation under vacuum. The residual viscous material, soluble in pyridine and chloroform, contained a single isomer (A) of bis(4-*tert*-butylcyclohexyl)thallium chloride that could not be isolated in pure form. On standing, the viscous material deposited a solid devoid of the organothallium compound (probably thallous chloride).

Analysis: calculated for $C_{20}H_{38}TlCl$, C 46.34, H 7.39, Cl 6.84, Tl 39.43; found (isomer A), C 57.78, H 9.13, Cl 3.5, Tl 25.05%; calculated for $C_{20}H_{38}$ (4,4′-di-*tert*-butylbicyclohexyl), C 86.52, H 13.48; found C 86.37, H 13.96%. IR (film) 2940 (asym. aliphatic C–H stretch), 2850 (sym. aliphatic C–H stretch), 1450 (asym. bending, C–H def.), 1395 and 1370 cm^{-1} [CH_3 sym. bend (doublet) *tert*-butyl], 1255 and 1235 (skeletal vibs.)

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REFERENCES

1. F. R. Jensen and C. H. Bushweller, *Adv. Alicyclic Chem.* **3**, 139 (1971); J. Hirsch, *Top. Stereochem.*, edited by E. L. Eliel and N. L. Allinger, Wiley–Interscience, New York, **1**, 199 (1967).
2. F. R. Jensen, C. H. Bushweller and B. H. Beck, *J. Am. Chem. Soc.* **91**, 344 (1969).
3. F. R. Jensen and L. H. Gale, *J. Am. Chem. Soc.* **81**, 1261 (1959).
4. F. R. Jensen and L. H. Gale, *J. Am. Chem. Soc.* **81**, 6337 (1959).
5. F. A. L. Anet, J. Krane, W. Kitching, D. Doddrell and D. Praeger, *Tetrahedron Lett.* 3255 (1974).
6. P. F. Barron, D. Doddrell and W. Kitching, *J. Organomet. Chem.* **139**, 361 (1977).
7. B. V. Cheesman, PhD Thesis, City of London Polytechnic (1980).
8. J. P. Maher and D. F. Evans, *J. Chem. Soc.* 637 (1965).
9. R. U. Lemieux, R. K. Kullnig, H. J. Bernstein and W. G. Schneider, *J. Am. Chem. Soc.* **80**, 6098 (1958).
10. H. Booth, *Prog. Nucl. Magn. Reson. Spectrosc.*, edited by J. W. Emsley, J. Feeney and L. H. Sutcliffe, Pergamon Press, Oxford, **5**, 149 (1969).
11. R. C. Weast (Ed.), Handbook of Chemistry and Physics, 62nd ed., p. E52. CRC Press, Boca Raton, FL (1981–82).
12. G. Wood, E. P. Woo and M. H. Miskow, *Can. J. Chem.* **47**, 429 (1969).
13. R. D. Stolow and T. Groom, *Tetrahedron Lett.* 5781 (1968).
14. I. Shukoff, *Chem. Ber.* **38**, 2691 (1905).

15. A. J. Berry and T. M. Lowry, *J. Chem. Soc.* 1748 (1928).
16. F. Challenger and O. V. Richards, *J. Chem. Soc.* 405 (1934).
17. E. Krause and A. von Grosse, *Chem. Ber.* **58**, 1933 (1925).
18. H. Hartmann and G. Bäthge, *Angew. Chem.* **65**, 107 (1953).
19. M. M. Kreevoy and J. F. Schaefer, *J. Organomet. Chem.* **6**, 589 (1966); V. G. Gibb and L. D. Hall, *Carbohydr. Res.* **50**, C3 (1976); **55**, 239 (1977).
20. *Beilsteins Handbuch der Organischen Chemie*, Zweites Ergänzungswerk, **5**, 43, Berlin (1943).
21. H. Adkins and A. K. Roebuck, *J. Am. Chem. Soc.* **70**, 4041 (1948).
22. I. B. Douglas and B. S. Farah, *Org. Synth.* **40**, 62 (1960).
23. S. I. Goldberg and M. S. Sahli, *J. Org. Chem.* **32**, 2059 (1967).
24. U. Kh. Agaev, S. Z. Rizaeva, A. T. Aliev and Yu. A. Pentin, *Azerb. Khim. Zh.* **4**, 16 (1972).
25. J. B. Lee and I. M. Downie, *Tetrahedron* **23**, 359 (1967).
26. M. Mousseron and R. Granger, *C.R. Acad. Sci.* **206**, 1489 (1938).
27. F. D. Greene, C. C. Chu and J. Walia, *J. Org. Chem.* **29**, 1285 (1964).
28. E. L. Eliel and R. S. Ro, *J. Am. Chem. Soc.* **79**, 5995 (1957).
29. E. L. Eliel and R. J. L. Martin, *J. Am. Chem. Soc.* **90**, 689 (1968).
30. J. R. Hall and M. K. Wilson, *Spectrochim. Acta.* **22**, 1729 (1966).

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