THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF THALLIUM ALKYLS AND RELATED COMPOUNDS.

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TO THE FAMILY.

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Le thallium est destiné à faire époque dans l'histoire de la chimie par l'etonnant contraste qui se manifeste entre ses caractères chimiques et ses propriétés physique. Il n'y a pas d'exagération à dire qu'on point de vue de la classification généralement acceptée pour les métaux, le thallium offre une réunion de propriétés contradictoires qui autoriserait à l'appeler le métal paradoxal, l'ornithorrhynique des métaux.

J. B. A. Dumas.

The desire to experiment is like fire in the blood.

Lady Gregory.

ABSTRACT.

Various aspects of the proton magnetic resonance spectra of alkyl and aryl thallium compounds have been studied.

It was shown that in trimethyl thallium in tolueneα-d_3 solution, that the intermolecular exchange of methyl groups follows second order kinetics and has an activation energy of 6.3 ± 0.5 k.cals. A mixed tri(methyl,vinyl) thallium has been prepared in which a very rapid exchange of the vinyl groups occurs; at low temperatures the mixed species Me_2ViTl and $MeVi_2Tl$ were characterised. It was also possible to demonstrate the presence of the mixed alkyls Me_2EtTl and $MeEt_2Tl$ in mixtures of trimethyl and triethyl thallium at -80° . The effect of trimethylamine and dimethyl ether in slowing down these exchanges, and the corresponding exchange of phenyl groups in triphenyl thallium, has been studied. This effect is particularly marked with triphenyl thallium, and a stable adduct $Ph_3Tl.NMe_3$ has been prepared.

A large number of $Tl^{203/205}$,H spin-spin coupling constants in organo-thallium compounds have also been studied. It was demonstrated that the Tl,H coupling constants vary in a similar manner to the corresponding H,H coupling constants, but are larger by a nearly constant factor. The variation of the Tl,H coupling constants in the series R_3Tl, R_2Tl^+ and RTl^{2+}, can be explained on the basis of the variation in the s-character of the Tl-C bond and the changes in the effective nuclear charge of the thallium atom. This observation, and the similarity between the Tl,H and the H,H coupling constants leads to the conclusion that the Tl,H coupling constants are, like the H,H coupling

constants, dominated by the Fermi contact interaction mechanism.

Some evidence is also presented which suggests that the compound $PhTlCl_2$ probably has a linear species $(PhTlCl)^+$ in the solid state and in certain solutions.

During the study of the Tl,H coupling constants some new compounds were characterised.

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INTRODUCTION.

Organo-thallium compounds.

Thallium forms a diversity of organometallic compounds, widely differing in properties and stabilities. The lower trialkyl thalliums, such as Me_3Tl are reactive, unstable to heat and light and spontaneously inflammable in air. They may conveniently be handled by vacuum line techniques being either low melting solids or liquids, with vapour pressures of a few millimeters. They are soluble in organic solvents but react with solvents such as dichloromethane and carbon disulphide. These trialkyls become less stable as the size of the alkyl chain is increased.

The triaryl thalliums are white, crystalline and involatile solids which are slowly oxidised in air and are more thermally stable than the trialkyls. They are soluble in polar organic solvents.

The hydrolysis of these trialkyls and triaryls give cationic species such as Me_2Tl^+ and Ph_2Tl^+ ; only one of the alkyl (aryl) groups is lost. The properties of these monovalent cations are somewhat similar to those of the Tl^+ and Ag^+ cations. Their halides are very stable (Me_2TlCl decomposes at ca 300°C), and are not hydrolysed by water and dilute acids; they form white iridescent crystals which can be crystallised from aqueous ammonia or pyridine. Dialkyl thallium sulphates, perchlorates and nitrates are moderately soluble in water, although their solubility decreases as the size of the alkyl is increased. Again the relative stability of these cations decreases as the size of the alkyl chain increases. X-ray (1) and Raman (2) measurements support a linear configuration (with an sp-hybridised thallium-carbon bond) for the ions $R - \overset{+}{Tl} - R$, these are isoelectronic

with the dialkyl mercurys.

Another aryl group may be removed from the di-aryl thallium cations by means of a disproportionation reaction with thallic chloride or bromide; an excess of thallic chloride is necessary to push the equilibrium over to the right hand side,

$$TlCl_3 + Ph_2TlCl \rightleftharpoons 2\ PhTlCl_2.$$

The monoaryl cations are more soluble in water than the diaryl cations, but they are not as stable, and their sulphates, perchlorates and nitrates readily disproportionate to the corresponding diaryl cation. They react with potassium iodide (to give the aryl iodide and thallic iodide), and also with solvents such as acetone (where the diaryl cations are formed). The stability of these aryls seems to increase as the size of the aryl is increased; for instance 1-napthyl thallium dichloride does not react with acetone. The existance of the mono-alkyl thallium species such as $MeTl^{2+}$, although reported by Russian workers (3) has recently been questioned (4); it was not possible to detect them in this work. Some of the substituted monoalkyls have however been isolated as intermediates in the oxidation of olefines with thallic acetate in the absence of water (5).

Preparations. Di-alkyl and di-aryl thallium bromides are formed by reacting thallic bromide or chloride with the corresponding Grignard reagent in ether (6) or tetrahydrofuran:

$$TlBr_3 + R_2Mg.MgBr_2 = R_2TlBr + 2MgBr_2$$

The trialkyl and triaryl thalliums are subsequently prepared by

reaction with the corresponding lithium alkyl (7).

$$LiR + R_2TlBr = R_3Tl + LiBr$$

Although the monoaryl di-cations can be prepared by disproportionation, it is easier to obtain them free from the diaryl cation by reacting an aryl boronic acid with thallic bromide or chloride in boiling water (8),

$$\varphi B(OH)_2 + TlCl_3 + H_2O = HCl + B(OH)_3 + \varphi TlCl_2$$

However some of the boronic acids, such as α-thiophene boronic acid, give the diaryl thallium chlorides .

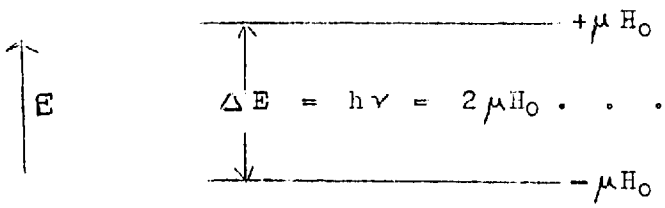
An additional method for preparing the dialkyl thalliums is by the reaction of thallic chloride with a dialkyl mercury e.g.,

$$2(CHCl{=}CH)_2Hg + TlCl_3 = (CHCl{=}CH)_2TlCl + 2(CHCl{=}CH)HgCl$$

(cf Nesmeyanov et al (9)).

Nuclear Magnetic Resonance.

An isolated nucleus with a nuclear spin $I = \frac{1}{2}$ may have two orientations, as allowed by the quantum theory, when placed in a magnetic field; these correspond to two nuclear Zeeman energy levels. The normal convention is that the magnetic field is taken in the negative z-direction so that when $I = -\frac{1}{2}$ the nucleus can be considered lined up with the field, and when $I = +\frac{1}{2}$, against the field. It is convenient to write α for the wave function in which $I_z = +\frac{1}{2}$, and β for the wave function in which $I_z = -\frac{1}{2}$. The nucleus also has an associated magnetic moment μ , so that the allowed energies of the two orientations in the field H_o are $+\mu H_o$ and $-\mu H_o$.



(1)

The energy separation ΔE of the two levels is then $2 \mu H_o$, and the frequency of the radiation required to induce transitions between them ν, is $h\nu = 2 \mu H_o$. The magnetic moment and the spin of the nucleus can be combined in the empirical equation

$$\mu = \gamma (I\hbar) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where γ, called the magnetogyric ratio, is a constant depending upon the particular nucleus. $\hbar = h/2\pi$ is the quantisation condition. Hence

$$h\nu = 2 \gamma I\hbar . H_o$$

$$\nu = \frac{\gamma H_o}{2\pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

For magnetic fields of the order of 10,000 Gauss these transitions lie in the radio frequency spectrum (I - 50 Mc/s)[10]

In the solid state the field at a nucleus is different from the field H_o, due to the magnetic fields of neighbouring nuclei, and differing nuclei will experience different fields covering a range of values. This causes resonance to occur over a range of frequencies so that only broadened spectral lines are observed. In a liquid or gas these magnetic dipole interactions are averaged to zero by the rapid molecular motions, and the resonance lines become very much sharper.

The circulation of electrons induced about a nucleus by the magnetic field, causes an induced secondary opposing field at the nucleus. This is expressed as

$$H_{nucleus} = H_o(1 - \sigma)$$

Where σ, called the screening constant, reflects the size of this field, and hence the amount of screening of the nucleus by its electrons.

Thus σ depends upon the chemical environment of the nucleus, so that different resonances will be observed for different chemically placed nuclei in a molecule. Chemical shifts were first observed for the protons in alcohols by Arnold, Dharmatti and Packard in 1951 (11). Since σ refers to the shielding of a bare nucleus it is not normally possible to measure it directly. From (3) the magnitude of the chemical shift is directly proportional to the applied field, and a non-dimensional unit δ is defined as,

$$\delta = \frac{H - H_r}{H_r}$$

and measured in parts per million. H is the resonant field of the signal being measured, and H_r is that for a reference signal. The reference compound is either mixed with the sample as an internal reference, or contained in an external reference tube. In proton resonance spectra in organic solvents, tetramethyl silane (T.M.S.) is used and arbitarily assigned a chemical shift (τ) of 10.0 p.p.m. to high field; in water the chemical shifts are commonly measured with respect to the methyl resonance of t-butanol.

The n.m.r. spectra of many molecules may show fine structure arising from spin-spin interactions between unequivalent magnetic nuclei. It was proposed by Gutowsky, McCall and Slichter, and by Hahn and Maxwell (12) that these interactions were proportional to the product of the nuclear moments. If for two nuclei A and X, these are μ_A and μ_X, then, using equation (2),

$$-K_{AX}\mu_A\mu_X = \gamma_A\gamma_X K_{AX}\hbar^2 I_A \cdot I_X$$

The spin-spin coupling constant is defined as

$$J_{AX} = \gamma_A \gamma_X h^2 K_{AX} \quad .$$

J_{AX} is a measure of the energy of interaction between A and X (with this sign convention J_{AX} is positive when anti-parallel nuclear spins have a greater stability than parallel spins [See Appendix II]). J_{AX} is independent of the magnetic field and is usually expressed in cycles/sec.. For a set of n_A equivalent nuclei of type A and n_X nuclei of type X, the A signal has $2n_X I_X + 1$ components and the X signal $2n_A I_A + 1$ compnnents. This gives the so-called 'first order' splitting, where the relative intensities of each group of signals are in the ratio of the corresponding binomial coefficients. If A and X refer to the same magnetic species, then these signals correspond to the chemically shifted positions of the nuclei, and the rules for predicting the number and intensity of the lines in the spectrum apply strictly only when the groups are widely separated ($J \gg \delta$). When $J \approx \delta$ second order splittings, which depend upon the field strength, make a simple first sight analysis of the spectrum impossible and mathematical methods must be used (see P.L.Corio (13), and J.A.Roberts (14)).

The spectrum can be altered by various rate processes (10), thus chemical exchange between two species with different chemical shifts (if the exchange is sufficiently rapid) effects a coalescence of the signals and only a single resonance is observed. This arises from an averaging of the nuclear environments and is a consequence of the uncertainty principle, $\Delta E . \tau_e \approx h \approx h \Delta\nu . \tau_e$ & $\tau_e \Delta\nu \approx \frac{1}{2\pi}$

where $\Delta\nu$ is the separation of the corresponding resonances and τ_e is the smallest time for which the two separate states are distinguishable. In the same way chemical exchange may remove the spin-spin splittings between two nuclei [See Appendix I].

The Proton Resonance Spectra of the Alkyl Thallium compounds.

Thallium has two isotopes, both with nuclear spin $\frac{1}{2}$, and with very similar nuclear magnetic moments: Tl^{203} (29·52% abundant, μ = 1·5960) and Tl^{205} (70·48% abundant, μ = 1·6114) (10). These isotopes produce large spin-spin splittings in the proton resonance spectra of the organo-thallium compounds. Because of the great simplicity of these spectra, due to the large and nearly equal magnetic moments of the thallium isotopes, the (usually) large coupling constants, and the lack of any naturally occuring isotopes without a spin $\frac{1}{2}$ (a factor which complicates Sn, Hg and Pb spectra), these compounds form an ideal series for studying heavy metal-proton spin-spin coupling constants.

The coupling constants for the isotopes Tl^{203} and Tl^{205} differ by only 1·04%, so that except for large coupling constants ($>$ 400 cycles/sec.) it is often not possible to distinguish between them. It is a fair assumption in these cases that the coupling constant which is measured refers to the Tl^{205} isotope since this resonance has the greater intensity. The chemical shifts of these alkyls and aryls are characteristic of the unsubstituted hydrocarbons cf for aliphatic protons τ = 8·0 $\rightarrow$ 9·5, for aromatic protons τ = 2 $\rightarrow$ 3 .

CHAPTER 1 ALKYL EXCHANGES.

Trimethyl thallium exchange.

In solvents such as dichloromethane and benzene the proton magnetic resonance spectra of trimethyl thallium show only a broad line at room temperature, whereas we should expect to see a doublet from spin-spin coupling between the thallium isotopes and the methyl protons. If the temperature of the sample is lowered the observed line broadens and then splits up into a doublet, until at $\sim -50^{\circ}C$ two proton resonance peaks separated by 250.4 c/sec are observed (the separate Tl^{203} and Tl^{205} splittings are not properly resolved). This shows that a rapid chemical exchange of the methyl groups is occuring at room temperature, and that by lowering the temperature the rate of exchange has been slowed down.

The separations of the two broad peaks were measured over a range of temperatures ($+20^{\circ}C$ to $-50^{\circ}C$) for two different concentrations of trimethyl thallium in toluene α-d_3. The exchange rates were calculated from the equation,

$$\frac{\text{Separation of peaks}}{\text{Separation of peaks for large } \tau} = \left[1 - \frac{1}{2\pi^2 \tau^2 (\nu_A - \nu_B)^2}\right]^{1/2} \quad (1)$$

where $\tau_{1/2}$ is the mean lifetime of the methyl groups between exchanges, and $(\nu_A - \nu_B)$ refers to the separation of the spin-spin doublet in the absence of exchange. (See Appendix 1.)

If the exchange is treated as a typical rate process, then the temperature dependence of the rate constant k is given by the Arrhenius

equation

$$k = k_o e^{-E/RT} \quad . . . . . (2)$$

where k_o is a constant and E the activation energy of the exchange. The specific rate constant $k = 1/\tau$. From equation (2),

$$\log_{10} 1/\tau = \log_{10} k_o - \frac{E}{2.3RT}$$

Figure 1 shows a plot of $\log_{10} 1/\tau$ against $1/T$. The slope of these lines gives an activation energy of 6.3 $\pm$ 0.5 k cals for the intermolecular methyl exchange. The equations to these lines, calculated by the method of least squares are

A (3.46 Molar) $\log_{10} 1/\tau = 8.079 - 1.42_4 \times 10^3 \, T^{-1}$

B (1.80 Molar) $\log_{10} 1/\tau = 7.470 - 1.33_4 \times 10^3 \, T^{-1}$

A study of this exchange was also carried out in dichloromethane, in this solvent an activation energy of 6 $\pm$ 1 k.cals. was obtained. However, even at low temperatures the solutions decomposed rapidly to give dimethyl thallium chloride. This could have influenced the activation energy by the formation of catalytic impurities. The very similar values for the activation energy in toluene and dichloromethane, indicate that this was not the case.

If the rate of methyl exchange is r , and the concentration is c, then

$$r = k_n c^n$$

where k_n is the velocity constant for the exchange. For two concentrations c_1 and c_2 , whose respective rates are r_1 and r_2 (at the same temperature), the order of reaction

$$n = \frac{\log_{10} (r_1/r_2)}{\log_{10} (c_1/c_2)} = \frac{\log_{10} (\tau_2/\tau_1)}{\log_{10} (c_1/c_2)}$$

For the solutions of trimethyl thallium in tolueneα-d_3 n = 2.0. In order to check this value the spectra of four solutions of different concentrations of trimethyl thallium in benzene-d_6 were observed at 26°C. The experimental line shapes were compared with the theoretical shapes calculated from the shape function (Appendix 1)

$$g(\nu) = K.\frac{\tau(\nu_A - \nu_B)^2}{\left[\frac{1}{2}(\nu_A - \nu_B) - \nu\right]^2 + 4\pi^2\tau^2(\nu_A - \nu)^2(\nu_B - \nu)^2} \quad (3)$$

where K is a normalising constant. The results are shown in Table 1. From the plot of $\log_{10}\tau$ against $\log_{10}(Me_3Tl)$, a value of $1.8_4 \pm 0.3$ is derived for the order of reaction. (The concentration of trimethyl thallium is represented: (Me_3Tl)). Thus, within the limits of the experimental error, the exchange is second order in both tolueneα-d_3 and in benzene-d_6. The exchange can be represented,

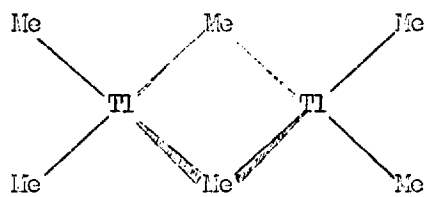
$$\frac{d(Me_3Tl)}{dt} = -k_2(Me_3Tl)^2 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The second order rate constant is related to τ by the equation,

(See Appendix I.)
$$k_2 = \frac{6}{\tau(Me_3Tl)}$$

At 26°, $k_2 = 3.43 \pm 0.06 \times 10^3$ litre. $mole^{-1}.sec^{-1}$ in tolueneα-d_3 ; and $9.4 \pm 0.6 \times 10^3$ litre.$mole^{-1}.sec^{-1}$ in benzene-d_6.

It is likely that a dimeric transition state is involved, this can be represented,



This methyl bridged dimer is analagous to the stable trimethyl aluminium dimer (15). It is significant that in trimethyl indium, weak bridge bonds give a tetrameric structure (16), and that this alkyl exchanges rapidly with trimethyl and triethyl thallium. Trimethyl thallium is however monomeric in benzene by freezing point experiments (17).

Table 2. shows results for trimethyl thallium in dimethyl ether and trimethylamine. In both cases the exchange rates have been slowed down compared to that in benzene-d_6. This can reasonably be attributed to weak complex formation between the two components, and an unstable complex $Me_3\bar{T}\dot{l}.\dot{N}Me_3$, m.p. $\sim 0^{\circ}C$ is known(17). The exchange of methyl groups between dimethyl zinc and dimethyl cadmium in various solvents has recently been studied by McCoy and Allred (18); no comparable effect of donor solvents was observed with these, this is consistent with the even lower tendancy of these alkyls to form complexes.

Triphenyl thallium exchange.

The spectrum of triphenyl thallium in dichloromethane is shown in Fig 2 (a). No thallium splitting is observed and the spectrum resembles that of a phenyl group in compounds such as nitrobenzene (an A_2B_2C - type spectrum (10)), indicating that a rapid intermolecular exchange of phenyl groups is occuring. In trimethylamine solution, Fig 2.(b), the exchange has been very considerably slowed down, and the ortho-, meta- and para-Tl,H coupling constants can be determined (Table 6(a))Because of the

overlap of groups B^1 and C^1, only approximate values for the meta- and para-Tl,H coupling constants could be obtained. Intermediate rates of exchange, giving broad featureless spectra, were observed in dimethyl ether and benzene-d_6 solutions of triphenyl thallium. From the values of the coupling constants in Table 6, it can be deduced that the average lifetime τ of the phenyl groups is > 0.05 sec. for the trimethylamine solution, and $< 3 \times 10^{-4}$sec for the other solutions. It is possible that the rates of phenyl exchange in these solutions may have been effected by catalytic impurities. However, the very large effect of trimethylamine as a solvent suggests that the triphenyl thallium complexes more strongly with trimethylamine than does trimethyl thallium. In agreement with this a stable complex $Ph_3\overset{-}{T}l.\overset{+}{N}Me_3$ was readily obtained on evaporation of a solution of triphenyl thallium in trimethylamine.

Triethyl Thallium exchange.

At room temperature a broad double line is observed in a toluene solution, on lowering the temperature to-60°C, this splits up into a double, triplet-quartet spectrum resembling that of the Et_2Tl^+ cation (Fig.10). The Tl,H coupling constants are given in Table 6(a) . No kinetic measurements were carried out on this species.

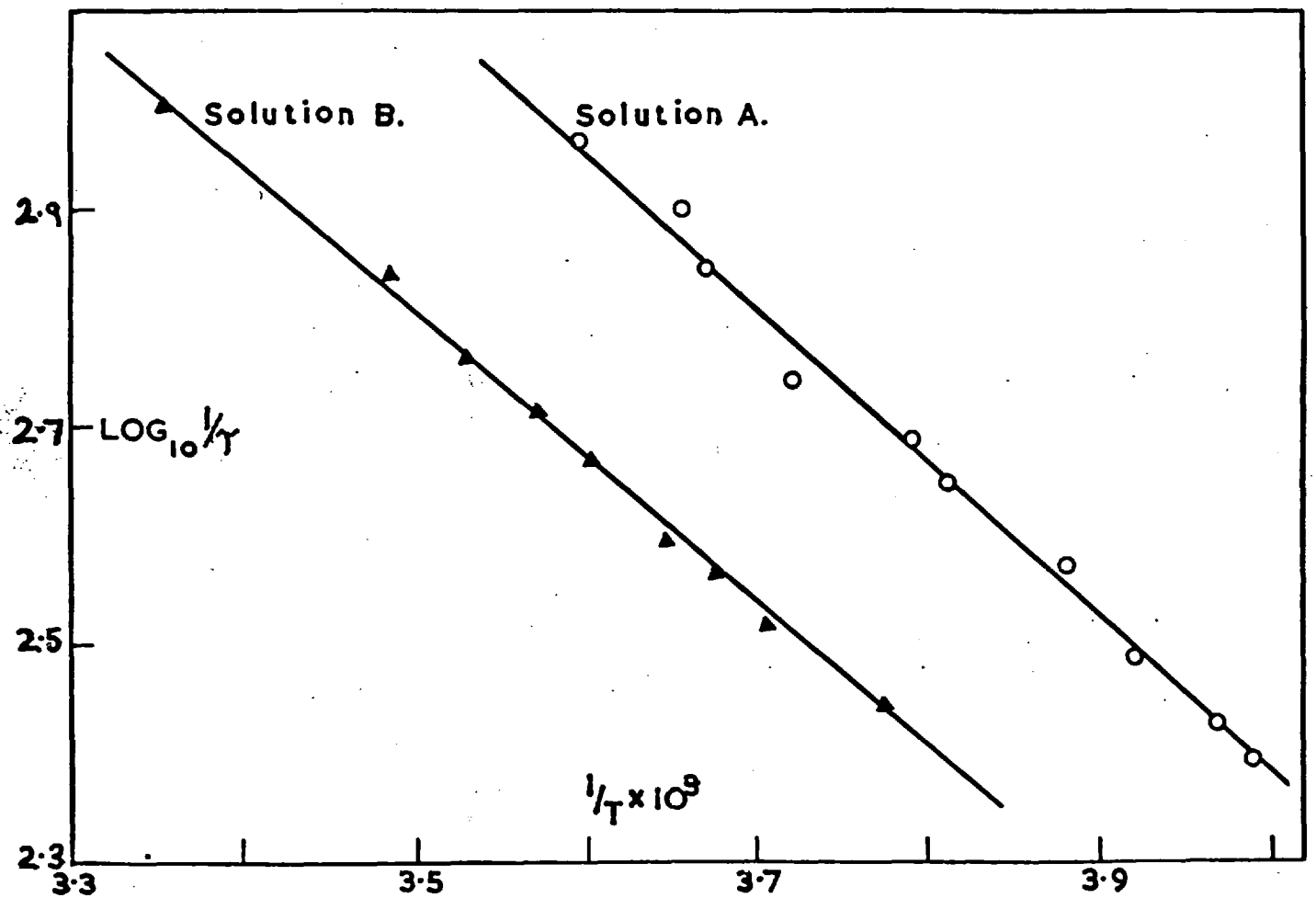


FIG 1. Temperature dependence of the exchange rates for solutions of Me_3Tl in toluene α-d_3.

Table 1.

Second-order rate constants, k_2 and τ values for solutions of trimethyl thallium in deuterobenzene at 26°C

$[TlMe_3]$ mol./litre	τ x 10^{-3} sec.	k, litre $mole^{-1}$ $sec.^{-1}$
0.31	1.85	10.4 x 10^3
0.46	1.30	10.1 "
0.96	0.78	8.0 "
1.22	0.54	9.1 "

Table 2.

Trimethyl thallium exchange in dimethylether and trimethylamine

Solvent	τ^* x 10^{-3} sec.	$[TlMe_3]$ mole $litre^{-1}$	$J(^{205}Tl-H)$ c./sec.†
Me_3N	3.86	0.74	271.5
Me_2O	3.25	1.65	269.5

* Calculated using equation (1); at 26°C

† At -60°C.

FIG 2.

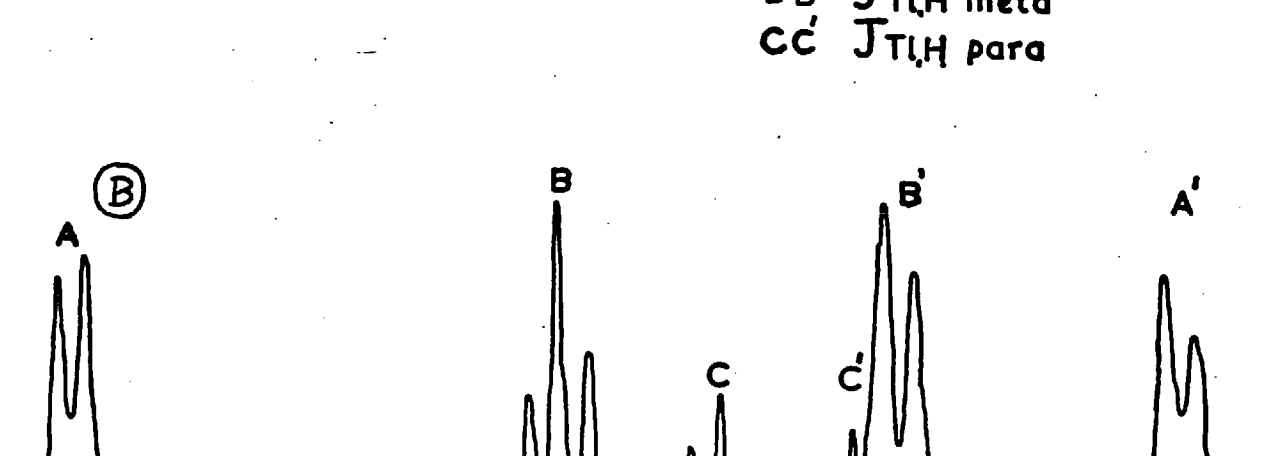


Thallium Triphenyl in

(A) Dichloromethane

(B) Trimethylamine

AA' $J_{Tl,H}$ ortho
BB' $J_{Tl,H}$ meta
CC' $J_{Tl,H}$ para



CHAPTER 11.

The Formation of Mixed Alkyls.

In 1934 Birch succeeded in preparing diethyl isobutyl thallium (19), but he was unable to characterise it adequately. The exchange of alkyl groups between two monomeric trialkyl thallium molecules should enable mixed alkyls to be prepared, it seemed probable that the mixed alkyls might give differing proton magnetic resonance spectra.

Trimethyl thallium / Triethyl thallium.

Mixtures of these alkyls in dichloromethane, when cooled to $-85^{\circ}C$, give proton resonance lines additional to those due to the pure trialkyls. By varying the relative initial concentrations of the alkyls, it was possible to detect the presence of Me_2EtTl in a solution rich in Me_3Tl, and $MeEt_2Tl$ in a solution rich in Et_3Tl. This is in agreement with the redistribution laws of Calingaert (20). An example of a typical spectrum is shown in Fig 3, and the spin-spin coupling constants and chemical shifts for all the four trialkyls Me_3Tl, Me_2EtTl , $MeEt_2Tl$ and Et_3Tl are shown in Table (3). It is seen that the detection of the mixed species relies on small changes in the Tl,H coupling constants, these will be discussed later. Chemical evidence for the formation of mixed alkyls was obtained by hydrolysing a mixture of trimethyl and triethyl thallium. This gave a solution containing the unsymmetrical cation $MeEtTl^+$ in addition to the Me_2Tl^+ and Et_2Tl^+ cations. This mixed species

was also detected by its proton resonance spectrum Fig 3b , the coupling constants are shown in Table 10 .

Trimethyl thallium / Trivinyl thallium.

Trivinyl thallium has not yet been prepared, and although all of the attempts to prepare this compound were unsuccessful, it was found that the reaction of methyl lithium with divinyl thallium chloride gave a mixed tri-(methyl,vinyl) thallium. The proton resonance spectra of solutions of this species are shown in Fig. 4. In the benzene-d_6 solution at 26°C, the methyl peak is broad, but the characteristic vinyl spectrum is extremely sharp and shows no evidence of spin-spin splitting by the thallium isotopes (Fig 4a); this is presumably due to a very rapid exchange of vinyl groups. However, in trimethylamine at 26°C the vinyl spectrum has started to broaden (Fig 4b) and the methyl peak splits into a broad doublet (not shown), the low field component being obscured by the trimethylamine resonance, showing that the exchange of both the methyl and the vinyl groups has been slowed down. In the vinyl part of the spectrum, lines 5,6,7,8, which show the greatest collapse, belong to the proton trans to the thallium, which by analogy with the coupling constants in Vi_2Tl^+ (see Table 6a) is expected to have the largest Tl,H coupling constant. This group will collapse before the others, since if the multiplet splitting $J_{Tl,H}$ is $(\nu_A - \nu_B)$ then it will start to reappear when $\tau \approx \frac{1}{2\pi(\nu_A - \nu_B)}$

At -64°C in trimethylamine, the vinyl spectrum cannot be detected, probably because the peaks have become too broad. However

the methyl part of the spectrum (Fig 4c) shows three well defined doublets, which, by analogy with the mixed $(Me,Et)_3Tl$ system, will correspond to the species Me_3Tl, Me_2ViTl and $MeVi_2Tl$. Similar effects were observed for dimethyl ether solutions of tri-(methyl,vinyl) thallium. The H,H coupling constants for the (exchanging) vinyl groups, making the assumption that in vinyl derivatives J trans > J cis > J gem (10) are shown in Table 3 alongside those for $(Vi)_4Sn$ $(Vi)_2Hg$ and $(Vi)_4Pb$. (Hg, Sn and Pb have nearly the same electronegativities as Tl so that their H,H coupling constants might be expected to have the same magnitudes. (21)).

The chemical shifts of the vinyl protons are concentration and solvent dependant, but for a 1·0 M solution (with respect to thallium) at 26°C are H_1 = 7·53; H_2 = 6·63; H_3 = 4·13; to low field of T.M.S.

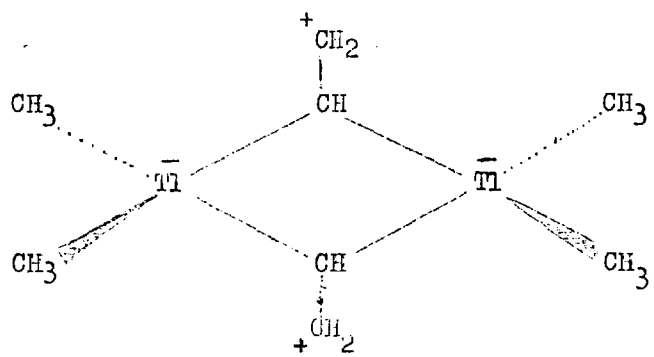


(The vinyl protons gave an AMX type of spectrum (14).)

The Tl,H(methyl) coupling constants at −64°C are shown in Table (4).

Schaeffer (21) and Banwell and Shoppard (22) have correlated the sum of the ethylenic H,H coupling constants (J gem + J cis + J trans) in a series of vinyl compounds, with the electronegativity of the substituent. Using their data, an electronegativity of 1.95 is obtained for thallium; this compares with a value of 2.05 for thallium in triethyl thallium, calculated using the Dailey-Schoolery equation (23).

It was estimated that the rate of methyl exchange for the 1.0.M solution of tri-(methyl,vinyl) thallium in benzene-d_6 at 26°C was approximately thirty times faster than for a solution of trimethyl thallium of the same concentration. The Tl,H coupling constants for the vinyl protons could not be determined, but from the values obtained for the divinyl thallium cation (Table 6(a)), and by analogy with the ratios observed between the coupling constants in the other organo-thallium compounds presented later, it can be estimated that the largest coupling constant $J_{Tl,H(trans)}$ is $\sim$ 1000 c/sec. Hence the vinyl exchange rate must be much more rapid even than the methyl exchange rate. This very rapid exchange of vinyl groups is at first sight rather surprising, since $p_\pi - p_\pi$ bonding (as postulated in the vinyl boranes (24) might be expected to slow down the rate of exchange. However, the transition state may be stabilized by the contribution of structures such as



to the resonance hybrid. Alternatively, donation of the π-electrons of the double bond into the vacant p-orbital of the thallium may occur. It is significant that very recently Oliver and Stevens (25) have shown that Vi_3Ga is dimeric in cyclohexane solution, whereas Et_3Ga is monomeric.

Thus a vinyl group may facilitate exchange by acting as a bridging group for the transition state, this would lower the activation energy and make exchange easier.

The possibility that the exchange involves free radicals was considered, however a sample of tri(methyl,vinyl) thallium did not initiate the polymerisation of styrene. The tri(methyl,vinyl) solutions slowly deposit thallium metal at room temperature; the proton resonance of the decomposed alkyl shows that it contains olefinic species of uncertain type with chemical shifts of 4.91 and 7.1 ppm. to low field of T.M.S., and some saturated hydrocarbon together with Me_3Tl.

The hydrolysis of tri,(methyl,vinyl) thallium gave only the Me_2Tl^+ cation, there was no evidence from the n.m.r. spectrum that the mixed species $MeViTl^+$ was formed. The vinyl groups in tri-(methyl,vinyl) thallium are probably hydrolysed faster than the methyl groups; also the Me_2Tl^+ cation is much more stable than the Vi_2Tl^+ cation.

Trimethyl thallium / Triphenyl thallium.

It was not possible to detect mixed species from the spectra of mixtures of triphenyl thallium and trimethyl thallium in dichloromethane or toluene, since triphenyl thallium crystalises, even from dilute solutions, on lowering the temperature of the sample. Neither was it possible to obtain the cation $MePhTl^+$ by hydrolysing a mixture of triphenyl thallium and trimethyl thallium (only a mixture of Me_2Tl^+ and Ph_2Tl^+ was obtained). An attempt to prepare $MePhTl^+$ by

the reaction of a mixture of phenyl and methyl magnesium bromides on thallic bromide gave only a mixture of Me_2TlBr and Ph_2TlBr. The reaction of phenyl thallium dichloride with ethyl magnesium bromide gave a mixture of Et_2Tl^+ and Ph_2Tl^+ halides. The species $PhMeTl^+$ is probably unstable and may disproportionate easily. (The mixed alkyl, aryl mercury compounds can only be prepared in the absence of alkyl mercuric halides which act as disproportionation catalysts (17).)

Alkyl Exchange amongst Group III Trialkyls.

The rate of exchange of the alkyl groups amongst these alkyls seems to depend upon their alkyl bridging properties. Thus it has been found (26) that the exchange rates decrease in the order

In/In In/Tl Tl/Tl Tl/B B/B

The trialkyl borons, unlike the trialkyl aluminiums, do not associate, and the exchange of alkyl groups does not take place below 100°C. However, if the alkyl is α-branched (eg. tri-isopropyl boron, tri-sec.butyl boron) the alkyl exchange occurs at a lower temperature, since these groups form bridged intermediates more easily than the straight-chain hydrocarbon trialkyl borons (27). The exchange of alkyl groups in the trialkyl borons is also strongly catalysed by traces of trialkyl aluminiums through the formation of bridged intermediates (17).

A mixture of triethyl boron and trimethyl thallium at low temperature (-100°C) does not exchange, however at room temperature the colourless solution rapidly turns yellow due to the formation of

triethyl thallium, and mixed tri-(methyl,ethyl) thalliums can then be observed at low temperatures. The exchange of alkyl groups between trimethyl and triethyl, indium and thallium, is rapid even at -100°.

In dimethyl zinc and dimethyl cadmium the rates of exchange of the methyl groups are slower than those for the Group III trialkyls (18); this is consistent with the even lower tendency of the Group II alkyls to form bridging dimers.

Table 3x.

H,H coupling constants in some metal-vinyl compounds.

Compound.	J_{cis} c/sec.	$J_{trans.}$ c/sec.	J_{gem} c/sec.	$\sum J.$	Electro-negativity (21)
$(Vi,Me)_3Tl$	12.8 ± 0.2	20.0 ± 0.2	4.3 ± 0.2	37.1	2.0
Vi_4Pb	12.1	19.6	2.0	33.7	1.9
Vi_2Hg	13.1	21.0	3.5	37.6	2.0
Vi_4Sn	14.1	20.3	2.8	37.2	2.0

See Table 9 (b).

Table 3.

Coupling constants and chemical shifts for trialkyl thalliums in dichloromethane at ca. -85°C.

Compound	Methyl group		Ethyl group			
	$J_{Tl,H}$ c/sec.*	τ (p.p.m.)	$J_{Tl,H(CH_2)}$ c/sec.*	τ_{CH_2} (p.p.m.)	$J_{Tl,H(CH_3)}$ c/sec.	τ_{CH_2} (p.p.m.)
Me_3Tl	250·8	9·48	-	-	-	-
Me_2EtTl	223·0	9·58	242·4	8·66	472·7	8·20
$MeEt_2Tl$	186·9	9·73	218·8	8·71	441·5	8.18
Et_3Tl	-	-	198·2	8·71	396·1	8·21

The $H_{(CH_2)},H_{(CH_3)}$ coupling constant was $7{\cdot}7 \pm 0{\cdot}3$ c/sec. in all the ethyl derivatives.

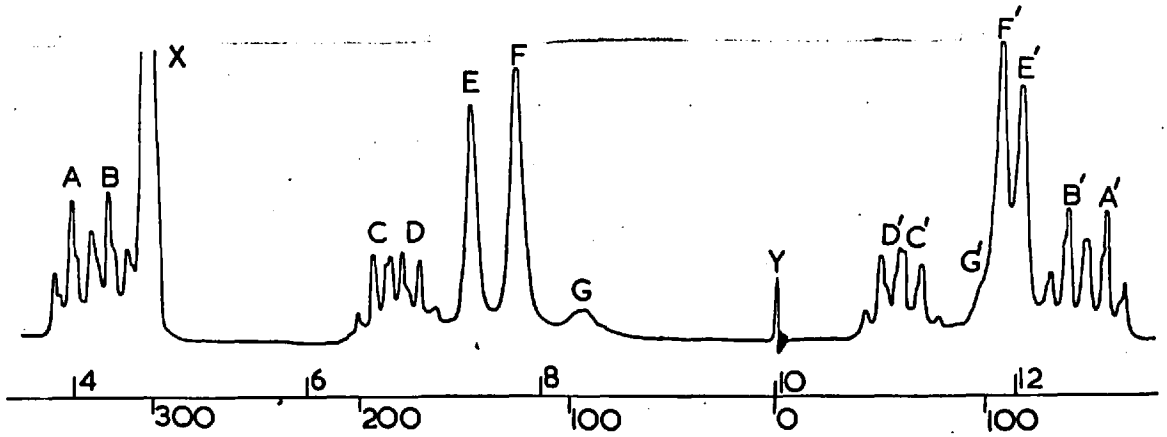
* These values will be slightly low (by 1~c/sec.) since the Tl^{205}/Tl^{203} splitting was not resolved.

Table 4.

$Tl,H_{(Methyl)}$ coupling constants for solutions of tri-(methyl,vinyl) thallium.

Compound	Solvent	
	Me_2O	Me_3N
Me_3Tl	269·6	270·3
Me_2ViTl	294·6	295·5
$MeVi_2Tl$	316·8	317·4

FIG 3a Mixture of Me_3Tl & Et_3Tl in CH_2Cl_2 at −85°.



Top scale — τ (ppm.). Lower scale — cycles/sec.

AA'·CH_3·Et
CC'·CH_2 } Me_2EtTl
FF' ····· Me

BB'·CH_3·Et
DD'·CH_2 } $MeEt_2Tl$
GG' ····· Me

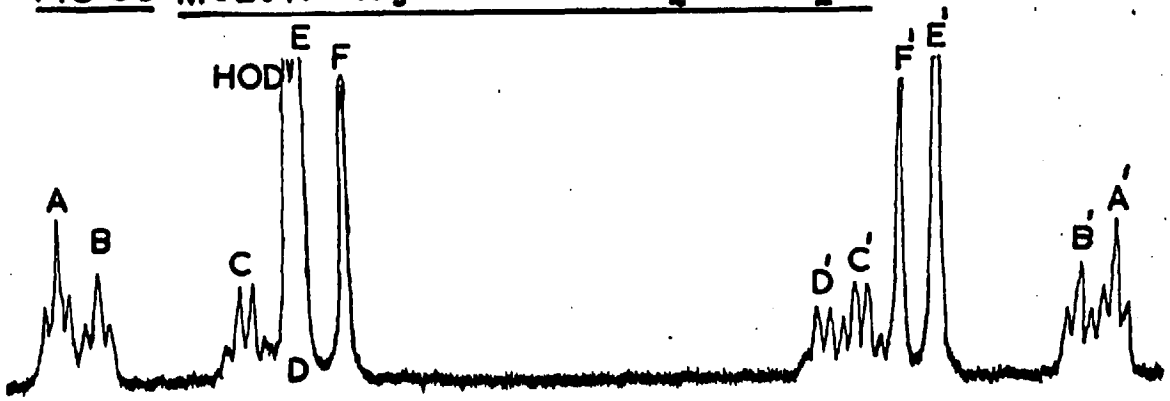
Me_4Si ····· Y

CH_2Cl_2 ····· X

EE' ····· Me_3Tl

There is considerable overlap of the lines arising from the Et groups. AA' & BB' show differential splitting by Tl^{203} & Tl^{205}.

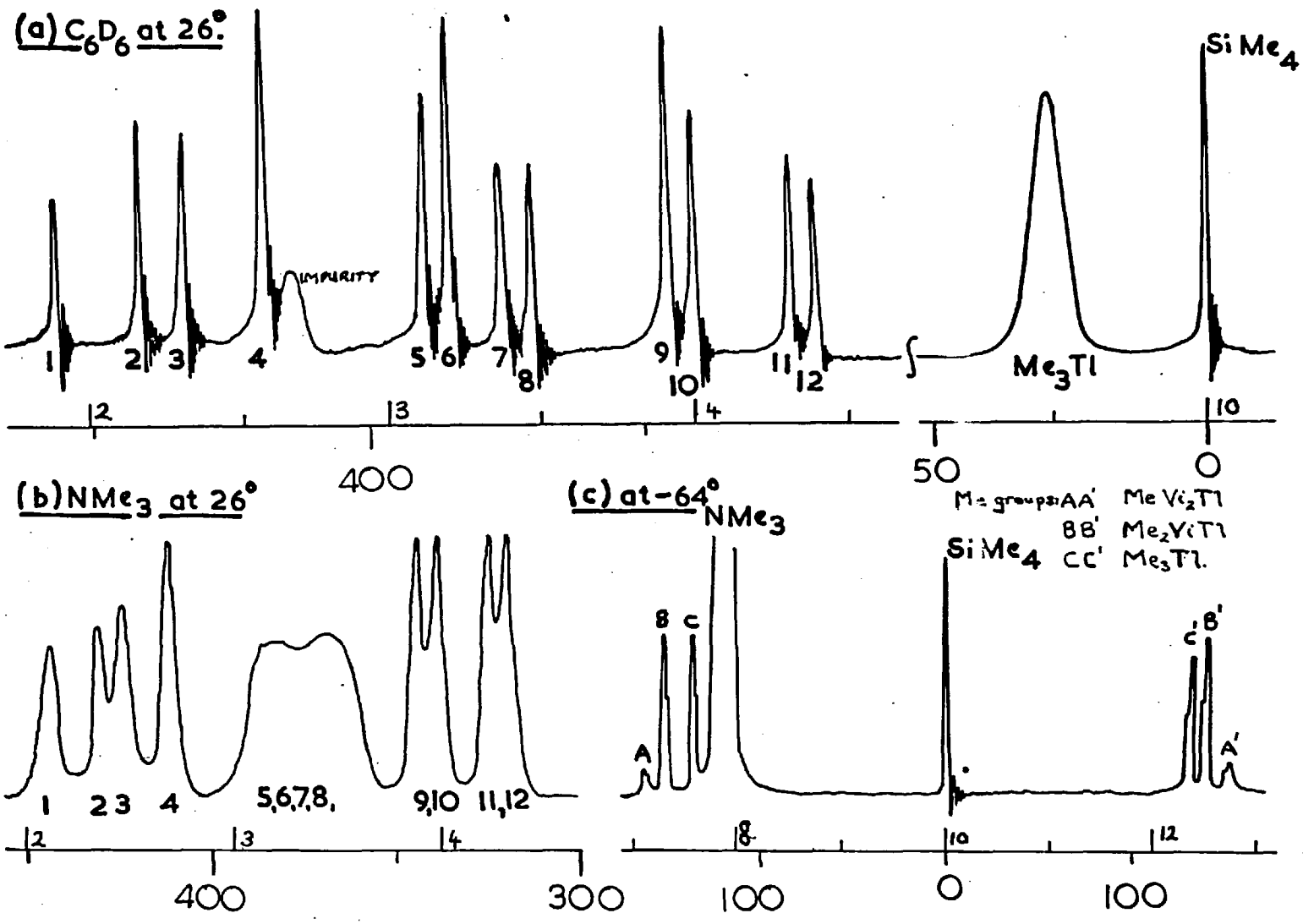
FIG 3b $MeEtTl^+$ together with Me_2Tl^+ & Et_2Tl^+



AA' CH_3 } Ethyl
CC' CH_2 }
FF' ····· Methyl
} $MeEtTl^+$

BB' CH_2 } Et_2Tl^+
DD' CH_2 }
EE' ····· Me_2Tl^+

FIG 4 Proton magnetic resonance spectra of solutions of tri(methyl,vinyl) thallium in, (1-12 vinyl group)



Top Scales = τ ppm. Lower Scales = c/sec.

CHAPTER III

Spin-Spin Coupling Constants.

Introductory. The general theory of nuclear spin-spin interactions was developed by Ramsey and others (28); it was shown that these interactions arise from an indirect coupling mechanism, via the bonding electrons in the molecule. The Hamiltonian describing the total coupling energy was derived by considering the contributions from three separate mechanisms:

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_3 .$$

$\mathcal{H}_1$ - the magnetic field of the nucleus interacts with the orbital motions of the electrons. The nuclear magnetic moment induces currents in the molecule setting up a secondary magnetic field which is experienced by the other nuclei. Thus the contribution from $\mathcal{H}_1$ is analagous to the chemical shift σ , and it can be related to the anisotropy of the screening constant. In H,H coupling constants the contribution from $\mathcal{H}_1$ is practically negligable, and in the coupling constants of other nuclei it has been shown to amount to only a few cycles/sec.(29).

$\mathcal{H}_2$ - the nuclear magnetic moments interact with the electronic magnetic moments in a dipole-dipole coupling. With H,H coupling constants this interaction has been shown to be relatively unimportant (10), since, like the coupling via the electron orbital motion $\mathcal{H}_1$, it involves p-,d-,and f-type atomic orbitals, whereas the electrons on a hydrogen atom are in a predominantly 1s-type atomic orbital. McConnell (30), found that $\mathcal{H}_1$ could be divided into two contributions, which arise from one and two electron parts in the molecular orbital equations. The one electron parts correspond to the nucleus perturbing its local electron cloud, so

causing a magnetic field which acts through space on the second nucleus. In the two electron parts the perturbation is passed through the bonds between the two nuclei. Thus the perturbation of the local electron cloud by the first nucleus affects the distribution of a second electron of a bonded atom, which in turn affects the electron distribution of another atom and so on to the second nucleus. In tetrafluoroethylene, Mc Connell found that one electron π -orbital contributions, proportional to the π -electron densities at the fluorines, can give a significant contribution to the coupling constant. However, the two electron intergrals, which are proportional to the π -bond order between these atoms probably make a negligible contribution to the coupling. These, and calculations of σ -bonded contributions from these terms, are difficult because of the unknown bond orders and amounts of sp-hybridisation in the system. Similar troubles beset all calculations of coupling constants.

$\mathcal{H}_3$. An electron in an s-type atomic orbital has a finite probability of being at the nucleus; this gives rise to the Fermi contact interaction (31). Since p-, d- and f-type atomic orbitals have zero probability of being found at the nucleus they cannot contribute to $\mathcal{H}_3$. The Fermi contact interaction provides most of the coupling energy in H,H coupling constants, and on this basis both valence bond (32) and molecular orbital (30) methods have been used to calculate these coupling constants Simple valence bond theory supposes that the pairing together of any two electrons in atoms A and B is sufficiently unique to render all other possible pairings irrelevant (33); were this strictly true, there would

be no means of interaction between magnetic nuclei of non-bonded atoms, and these coupling constants would be zero (34). However, the observation of these couplings is good evidence that there are (very small) deviations from perfect pairing. The valence bond method is particularly suited to calculations of the extent of non-perfect pairing of the bonding electrons, since the relative contributions from different valence bond structures can be considered.

Even in the simplest case, HD, where Ramsey (28) has shown that the predominant contribution is from the Fermi contact interaction, the agreement between experiment and theory, although apparently good, is based on an assumed value for the mean singlet-triplet excitation energy. This energy enters all the calculations of $\mathcal{H}_1$, $\mathcal{H}_2$ and $\mathcal{H}_3$, and because of the lack of knowledge of excited energy levels we can only make an intelligent guess as to its value.

Recently, several workers (35,36,37,38) have been able to correlate the amount of s-character on the carbon with the ' directly bonded ' C^{13},H coupling constants in various substituted methanes, ethylenes and acetylenes. These couplings were also found to depend upon the polarity and the length of the C-H bond. There is also reasonable agreement between the observed C^{13},H coupling constants and those calculated on the basis of the Fermi contact interaction (39,40).

The theoretical work for H,H coupling constants over more than one bond has met with mixed success; thus the valence bond calculations for vicinal H,H couplings through three bonds, in both saturated and unsaturated systems, assuming a Fermi contact interaction mechanism,

correlates well with the observed couplings and the observed change in the dihedral $H\diagdown C-O\diagup H$ angle (41). However, a similar calculation of the geminal H,H coupling over two bonds (41), although agreeing with the experimental magnitude of J has the wrong sign (42); it is possible that this situation might be altered by a better choice of the appropriate exchange integrals, especially since the theoretical value for J_{gem} involves two large, and almost self cancelling values for these exchange integrals.

In recent years there has been considerable interest in the coupling constants between protons and heavier magnetic nuclei of spin $\frac{1}{2}$, these are normally much larger than H,H coupling constants. Thus Narasimhan and Rogers (43) have found that in compounds of the type $(CH_3CH_2)_nX$ (X = P^{31}, $Sn^{117/119}$, Hg^{199} and Pb^{207}), J_{X,CH_3} is greater than J_{X,CH_2} and that these have opposite signs. The larger coupling to the more distant protons seems curious; this observation also provided the spur for the work presented here. Narasimhan and Rogers interpreted their results qualitatively in terms of McConnell's one electron terms, and also concluded that there was a large contribution from the Fermi contact interaction to J_{X,CH_3}, but that for J_{X,CH_2} other terms predominated. The coupling constants in some $(CH_3CH_2)_n$ X compounds are shown in Table 5. . On the other hand Stafford and Baldeschwieler (44) consider that the d-electrons, which may be involved in the bonding of these compounds, can cause changes in the magnitude and sign of the Fermi contact interaction, and may also provide another mechanism for the coupling. This contribution could be opposite in sign to the

contribution through the σ -bonds. Klose (45), in some recent valence bond calculations, based upon those of Karplus, for the vicinal H,H coupling constants, has shown that the magnitudes and signs of the X,H coupling constants can be accounted for on the basis of a Fermi contact interaction. It was found that the larger coupling over three bonds compared to that over two bonds could be explained theoretically by the choice of appropriate exchange integrals.

As with the C^{13},H coupling constants, a correlation between the s-character of the magnetic isotope X, and the X,H coupling constant is expected if this involves mainly the contact interaction. From Table 5 it is seen that $J_{X,H(CH_2)}/\mu_X$ decreases in the series Et_2Hg, Et_3Tl, Et_4Pb, where there is decreasing s-character in the metal-carbon bond; however, $J_{X,H(CH_3)}/\mu_X$ does not change very much. Holmes and Kaesz, on the basis of somewhat flimsy evidence, find a correlation between the percentage s-character in the Sn-C bond and the Sn^{119},H coupling constant in a series of methyl tin compounds (46).

In the work now presented the focus of attention is the great similarity between the H,H and the Tl,H coupling constants; thus the Tl,H coupling constants vary in the same manner as the H,H coupling constants but are larger by a nearly constant factor. Since the absolute signs of the coupling constants cannot be obtained, a positive sign is adopted for the vicinal Tl,H coupling constant, and, after Banwell and Sheppard (42), the same convention is used for the vicinal H,H coupling constants (see Appendix II).

* * * *

Table 5(a).

Coupling constants and other data for some methyl and ethyl compounds of magnetic isotopes with a nuclear spin of $\frac{1}{2}$.

Isotope	μ_x (10)	$(CH_3)_nX$	$\div\mu_x$	$J_{X,H(CH_2)}$ $(C_2H_5)_nX$	$\div\mu_x$	$J_{X,H(CH_3)}$	$\div\mu_x$	$Z_{eff.}$ (45)
H^1	2.793	12.4	4.5	-13.2	-4.4	+6.0 8.0	+2.5	1.0
C^{13}	0.702	4.1 - 5.6	6.8	-4.5	-6.4	+3.8 5.8	+6.8	3.25
N^{15}	-0.283	5.2	18.4	-	-	- -	-	3.90
F^{19}	2.627	11.0	4.2	± 46.7	±17.7	± 25.2	±9.6	5.2
Si^{29}	-0.555	6.8	12.4	-	-	-	-	4.15
P^{31}	1.131	2.7*	2.4	-0.5	-0.5	+13.7	+12.1	4.80
Se^{77}	0.533	11.2	21.0	-	-	-	-	6.95
$Cd^{111}/113$	-0.592 -0.619	50.2	83.7	+50.3	-84	-58.5	+97	4.35
$Sn^{117}/119$	-0.995 -1.041	53.1	52.1	+30.8 +32.2	-31.0	-68.1 -71.2	+68.5	5.65
Te^{125}	-0.882	20.7	23.5	-	-	-	-	6.95
Hg^{199}	0.499	102.0	204	-87.6	-175	+115.2	+221	4.35
$Tl^{205}/203$	1.596 1.611	250.8	156	-198	-123	+396	+246	5.00
Pb^{207}	0.584	60.5	104 †	-41.0	-70	+125	+214	5.65

If μ_x has a negative sign then there will be an apparent reversal of sign in columns 5 and 6.

The sources of this data are (43), (44), (45), *(14) Page 21, †(98).

Table 5(b)

Coupling constants in some vinyl compounds. (97).

Compound	$J_{M,H}$ trans	$J_{M,H}$ cis	$J_{M,H}$ gem
Vi_2Hg	295.5	159.6	128.5
Vi_3Tl*	950	475	495
Vi_4Sn	183.1	90.6	98.3

*Values for the coupling constants in Vi_2Tl^+ divided by 1.7 (see page 32).

The Variation of the coupling constants in the species R_3Tl, R_2Tl^+ and RTl^{2+}.

The uniform increase in the magnitude of the coupling constants through the series R_3Tl, R_2Tl^+ and RTl^{2+} is a general feature for all the organo-thallium compounds. This is shown in Table 6(a). If the predominant contribution to these coupling constants is from the Fermi contact interaction, then it might be expected that the coupling constants would be proportional to the s-character in the Tl-C bond. In addition, the wave function for an s-electron is proportional to $(Z_{eff})^3$ (33), where Z_{eff} is the effective nuclear charge; Z_{eff} will be increased for each positive charge on the atom.

The effective nuclear charge is calculated from the equation $Z_{eff} = (Z_o Z)^{\frac{1}{2}}$; where, for thallium Z = 81, is the real nuclear charge, and Z_o (= 5 for thallium in TlX_3) is the Slater screened nuclear charge (47), Z_o will increase by 0.65 units for each positive charge on the thallium. On this basis it would be expected that the coupling constants would be proportional to $(Z_o Z)^{3/2} S$, where S is the amount of s-character in the Tl-C bond. Assuming that S varies according to the ratios

$$R_3Tl \; : \; R_2Tl^+ \; : \; RTl^{2+} \;\; :: \;\; 0.33 \; : \; 0.5 \; : \; 1.0$$

the corresponding ratios obtained are

$$1 \; : \; 1.8 \; : \; 4.3 \;\; (\text{ or } 0.55 \; : \; 1.0 \; : \; 2.4 \;)$$

The average experimental ratios for the phenyl, vinyl, ethyl and methyl thalliums are shown in Table 6(b).

Such a calculation should not be taken too seriously since it does not take into account any changes in bond angles, bond distances, or possible changes in contributions from other terms to these coupling

Table 6(a)

Showing the variations in the Tl,H coupling constants between the three classes of alkyl thalliums, R_3Tl, R_2Tl^+ and RTl^{2+}.

R	Position	R_3Tl	R_2Tl^+	RTl^{2+}	
Phenyl	ortho	+ 259 †	+ 451 *	+ 948 *	c/sec.
	meta	+ 80±5	+ 139	+ 365	"
	para	+ 35±5	+ 51.7	+ 123	"
Vinyl	trans	–	+ 1618 *	+ 3750 *	"
	cis	–	+ 805 ±5	+ 1806 ±10	"
	gem	–	+ 842	+ 2004	"
Ethyl	CH_2	−198.2 °	− 340.4 *	–	"
	CH_3	+396.1	+ 628.0	–	"
Methyl	CH_3	−250.8 °	− 402.7 *	–	"

* as the perchlorate in D_2O .

† in trimethylamine.

° in dichloromethane.

Table 6(b)

The average ratios between the Tl,H coupling constants in Table 6(a).

R	R_3Tl	R_2Tl^+	RTl^{2+}
Phenyl	1	1.7	4.0
Vinyl	–	1 (1.7)	2.3 (3.9)
Ethyl	1	1.6	–
Methyl	1	1.65	–

constants. The calculation also makes the highly arbitary assumption that in RTl^{2+} the Tl-C bond has $\sim$ 100% s-character (see page 63). However as is seen from Tables 6(a) and (b), the agreement between the calculated and experimental ratios is very good, and does seem to indicate that the predominant contribution to all of these couplings comes from a Fermi contact interaction ($\mathcal{H}_3$).

The Phenyl Thalliums. (Table 6(a); Figs 2, 5 and 6.)

In substituted benzenes the ortho-, meta- and para- H,H coupling constants are, $J_{H,H\ ortho}$ = +6 to +9, $J_{H,H\ meta}$ = +1 to +3, $J_{H,H\ para}$ = 0 to +1 c/sec. (42). If the Tl,H couplings in $PhTl^{2+}$, Ph_2Tl^+ and Ph_3Tl are divided respectively by $\sim$130, $\sim$55 and $\sim$35, then the values obtained are very similar in both magnitude and sign, to the corresponding H,H coupling constants for the substituted benzenes.

Schneider and Buckingham (48) have pointed out that the contributions to the coupling constants from both $\mathcal{H}_2$ and $\mathcal{H}_3$ are approximately proportional to

$$\left\{\frac{Z_{eff}}{n}\right\}^3_N \left\{\frac{Z_{eff}}{n}\right\}^3_{N^*} \frac{\gamma^2_N \gamma^2_{N^*}}{\gamma^2_H}$$

for two different nuclei N and N^*; on this scale an H,H coupling constant = 1, n is the main quantum number (6s for thallium) and γ_N, γ_{N^*} and γ_H are the respective magnetogyric ratios. From this very simple approach we would expect the Tl,H couplings to be $\sim$ 50 times the H,H couplings. This is an extreme approximation which ignores differences in hybridisation, bond lengths, bond angles, and ionisation potentials, among other terms; it does, however, indicate that the greater

magnitude of the Tl,H couplings is largely accounted for by the larger effective nuclear charge of the thallium atom when compared to that of the hydrogen atom.

Mono-tolyl thallium di-cations. (Table 7, Fig 6).

In the cations $n\text{-}Pr_2Tl^+$ and $i\text{-}Bu_2Tl^+$ the couplings through four bonds to the γ $-CH_3$ are respectively 20.4 and 16.0 c/sec.(Table 10). In comparison with these couplings, both the meta and the para Tl,H couplings in Ph_2Tl^+ appear unusually large. It is possible that this is in part due to the geometry of the aryl system, but it might also come from a π -contribution to the coupling constant, as has been suggested by Hoffman to account for long range H,H couplings in various olefines and acetylenes (49). Previous to Hoffman's experimental work both McConnell (50) and Karplus (41) calculated the Fermi contact contribution from the π -electrons to the H,H couplings in unsaturated systems. Thus McConnell in a molecular orbital calculation used the proton hyperfine splitting constant Q, from the hyperfine structure of aromatic free radicals to calculate the contribution of the π -electrons to the inter-proton couplings in benzene and napthalene; he found a small coupling which was not rapidly attenuated with increasing bond distance between the protons. Karplus's valence bond method, which is based on $\sigma - \pi$ configuration interaction, requires that the substitution of a methyl group for an ethylenic proton will alter the sign but not the magnitude of the π -contribution. This is because $Q_{CH} \doteq Q_{CCH_3}$, but has an opposite sign. More recently, Acrivos has extended these calculations (51), he found that the experimental and

theoretical H,H coupling constants in mesitylene compared well.

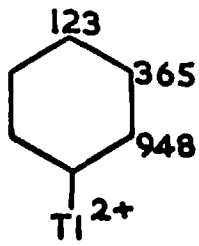
In the three mono-tolyl thallium di-cations, the Tl,H(CH_3) coupling constants are respectively 104.2, 50.1 and 60.0 $\pm$ 0.5 c/sec. for the ortho-, meta- and para substituted methyl groups. In mesitylene the ortho and para H,H(CH_3) coupling constants are respectively 0.89 and 0.45 c/sec, and again the Tl,H couplings are $\sim$ 130 times the H,H couplings. That the Tl,H(para) coupling constant is larger than the Tl,H(meta) coupling constant is consistent with Acrivos's calculations of the π -contribution to the H,H coupling constant (51) in mesitylene. There is as yet no experimental H,H(meta-CH_3) coupling constant available for comparison; however, in mesitylene Acrivos finds that J.H(CH_3), H(meta-CH_3) is less than 0.35 c/sec, thus the upper limit of the H,H (meta-CH_3) coupling can be assumed to be

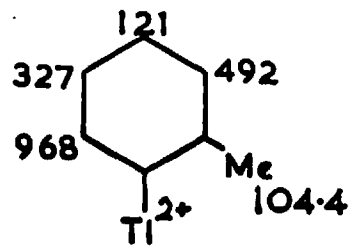
$$\frac{Q_{CH_3}}{Q_{CCH_3}} \times 0.35 \sim \frac{2.25}{27} \times 0.35 = 0.29 \text{ c/sec.}$$

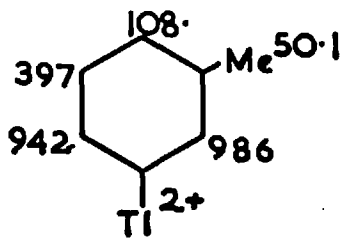
It is not possible to test the signs of the Tl,H(CH_3) couplings in any of these cations since there is no visible coupling between the ring protons and the methyl groups.

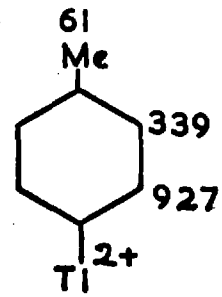
Thus the results suggest that as for the corresponding H,H coupling constants, the thallium coupling to the ortho and meta positions is transmitted mainly via the σ -bonds of the phenyl ring, but that for the para coupling there is a large contribution from the π -electron system (probably $>$ 50%). In addition to this, the Tl,H(meta) coupling constant, in the same manner as the H,H(meta) coupling constant appears anomalously large when compared to the analagous couplings over four bonds

TABLE 7



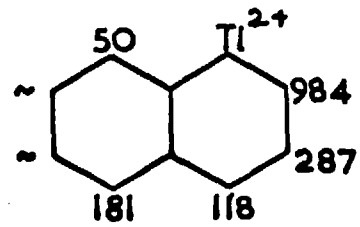


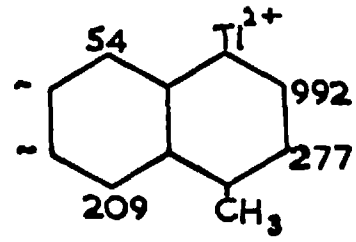


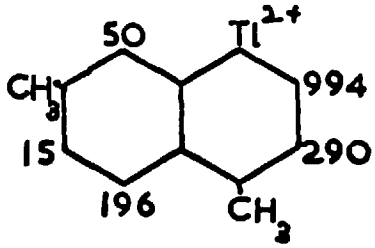


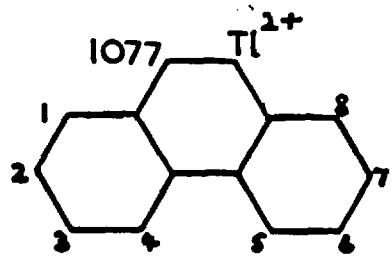
$J_{Tl,H}$ in ortho-, meta- & para- tolyl thallium di-cations

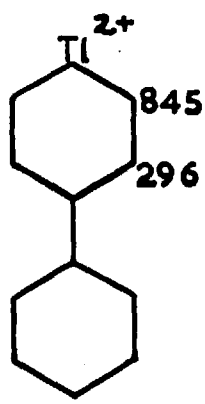
TABLE 8.



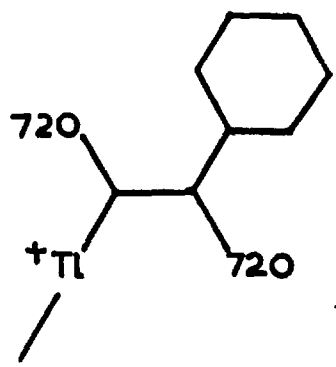








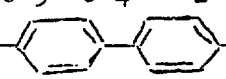
No coupling to far rings.



$J_{Tl,H}$ in some aryl thallium dichlorides and di-β-styryl thallium chloride

in saturated systems. Both of these couplings are at variance with the prediction, based on the Dirac vector model (50), that in a hydrocarbon chain the signs of the couplings should alternate along the chain.

The variations of the ring proton coupling constants with the different positions of the methyl groups in the phenyl ring (Table 7) do not seem to follow any definite pattern, except perhaps that the Tl,H(para) coupling remains more constant than the others, and that the Tl,H(meta) coupling varies most. The changes may reflect differences in the electron densities arising from an inductive effect for the methyl group competing with a mesomeric effect from the positively charged thallium.

The observation of the long range Tl,H(para) coupling made it conceivable that other longer range couplings would be observable over even greater numbers of bonds. However, no coupling was observable to the more distant phenyl ring in p-$C_6H_5.C_6H_4TlCl_2$ (Table 8). No inter-ring H,H coupling is observed in Cl--Cl (52).

1-Napthyl thalliums. (Table 8, Figs. 7 and 8).

Although no H,H coupling has yet been detected between the rings in Napthalenes (53) it might be possible with Tl,H couplings (since these are very much larger than the H,H couplings) to demonstrate the presence of inter-ring coupling, and then by dividing by ~ 130 (as for φTl^{2+}) to infer a possible magnitude for any inter-ring H,H coupling.

1.Napthyl thallium dichloride (15.7% by weight solution in dimethyl sulphoxide). This very amusing spectrum is shown in Fig 7 ; the

Tl,H coupling constants in the ring to which the thallium is attached may be assigned from the known couplings in mono-phenyl thallium dichloride, from their H,H coupling fine structure, and their intensities. They vary between the ortho-, meta- and para- positions in the same way as for mono-phenyl thallium dichloride. Besides these couplings, two other couplings appear (one component of these is hidden under the centre group(8)), and since these are both doublets from the H,H couplings they must correspond to the thallium coupling to H(5) and H(8). It is not possible on the basis of this spectrum alone to assign which is which; however from the spectrum of 4.7 dimethyl, 1-napthyl thallium dichloride (Fig 8b) they are assigned as $J_{Tl,H(5)} = 181.4$, $J_{Tl,H(8)} = 50$ c/sec. The coupling to H(5) is even larger than that to H(4), although these are both separated from the thallium by 5-bonds. Anomalously large H,H coupling constants have been found by several workers for protons which are connected by a similar "straight" bond path (42). Thus in quinoline Anet(54) found a coupling of 0.8 c/sec. between the 4- and 8- aromatic hydrogens; in various mono-methyl indenes a coupling of 0.7 c/sec. was found between the approximately trans-disposed 3- and 7- protons, and a similar coupling of 0.9 c/sec. was observed in benzofuran (55). The theoretical calculations of the π - contribution to the 1:5 and 4:5 H,H couplings in napthalene by McConnell (50) predict very much smaller coupling between these protons ($\sim$ 0.02 c/sec). Gutowsky and Porte have suggested that certain resonance structures, stabilised by the hetero-atom, are responsible for these couplings (56). That the H,H coupling is passed through the σ -bond

system in these compounds is supported by Elvidge and Foster's work on indenes (55), where, in agreement with Hoffman and Gronowitz's $C{=}C{-}H \rightarrow C{=}C{-}CH_3$ replacement criterion (49), the 3:7 H,H coupling disappears on substituting a methyl group in either the 3 or 7 positions. There are theoretical reasons (57) for believing that "straight" bond path configurations may be of particular stability, this could increase the σ-bonded coupling.

(It would be possible to check this for the 1,Napthyl thalliums by measuring the spectrum of 5,methyl,1-napthyl thallium dichloride; if the coupling is transmitted by the σ -bonds the Tl,H(5-CH_3) couplings will be very small compared to the (Tl,H(5) coupling. This work is in hand.)

The coupling to H(8) (which is separated from the thallium by the same number of bonds as the meta-proton), may have a large 'through space' contribution (cf McConnell's one electron parts) as it is particularly close to the thallium ($\sim$ 2.8 Å).

4-Methyl,1-napthyl thallium dichloride (Fig 8a). (19.6% by weight, solution in dimethyl sulphoxide). The spectrum of this compound confirms the assignment of the Tl,H(4) coupling made for the spectrum of 1-napthyl thallium dichloride. The Tl,H(5) and Tl,H(8) couplings have nearly the same values as in 1-napthyl thallium dichloride.

4,7,dimethyl 1-napthyl thallium dichloride (Fig 8b). (15.3% by weight solution in dimethyl sulphoxide). This spectrum indicates, that in addition to the Tl,H(5) and Tl,H(8) couplings, there is a very small coupling of $\sim$15 c/sec. to H(6). This may be representative of the

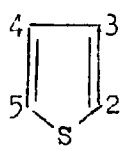
σ -contribution to the coupling to this ring.

The Tl,H(CH_3) couplings in these compounds were not measurable since they are obscured by the dimethyl sulphoxide signal. The spectra will be measured in dimethyl sulphoxide-d_6 and reported elsewhere.

9-Phenanthryl thallium dichloride (Fig 8c) (8.3% by weight, solution in dimethyl sulphoxide.) In this substance, although there is plainly coupling to either H(5) or H(8), the couplings are hidden under the centre broad resonance. It is also possible, though less probable, that H(1) and H(4) could couple to the thallium, these would also show a doublet H,H splitting. The Tl,H(ortho) coupling is the largest yet observed in these systems.

It is interesting that the Tl,H(ortho) coupling, like the corresponding H,H(ortho) couplings in benzene, napthalene and phenanthrene, increases from phenyl thallium dichloride (875 c/sec.), to 1-napthyl thallium dichloride (948 c/sec.), to 9-phenanthryl thallium dichloride (1077 c/sec.). In H,H coupling constants the corresponding increase parallels the increase in π-bond order calculated from simple molecular orbital theory, but is probably also accompanied by a change in the H,H distance (58).

Di-(α-thiophenyl) thallium sulphate. (Fig. 5). The coupling constants for this compound may be assigned using the fine structure from the H,H coupling constants in substituted thiophenes (49), these are



J_{23} = + 4.9 to + 5.8 c/sec. ; J_{24} = + 1.2 to + 1.7 c/sec.

J_{34} = + 3.4 to + 4.3 " ; J_{25} = + 3.2 to + 3.7 " .

The Tl(2), H coupling constants are:-

$J_{Tl,H(3)} = + 303.9$; $J_{Tl,H(4)} = + 104.6$; $J_{Tl,H(5)} = + 196.5$ c/sec.

Again, all of the Tl,H coupling constants have the same sign and are approximately 55 times the corresponding H,H coupling constants. It is of particular interest to find that the coupling through the hetero-atom ($J_{Tl,H(5)}$), is greater than the coupling through the ring carbon ($J_{Tl,H(4)}$), in the same manner as the corresponding H,H coupling constants in thiophene.

Vinyl thalliums. (Tables 5(a), 9(a); Figs. 9,11,12.)

In vinyl compounds $CH_2 = CHX$, the respective H,H coupling constants, which depend upon the electronegativity (E_x) of X are (21,42),

$$J_{trans} = + 19(1 - 0.17\ Ex) \quad . \quad . \quad . \quad . \quad A$$

$$J_{cis} = + 11.7(1 - 0.34\ Ex) \quad . \quad . \quad . \quad B$$

The ratios between the Tl,H and the H,H coupling constants for the cis and trans positions, are slightly larger than the ratios previously found between the Tl,H and the H,H coupling constants for the phenyl thalliums (thus in Vi_2Tl^+ : $J_{Tl,H} \sim 75 \times J_{H,H}$). The geminal H,H coupling constant in vinyl compounds varies greatly and depends upon the electronegativity of X, decreasing with increasing electronegativity. Thus for X = Li, $J_{gem} = + 7.1$ c/sec.(58); X = F, $J_{gem} = - 3.2$ c/sec.(59). The coupling can have either positive or negative values. When compared to the positive geminal H,H coupling constants, the geminal Tl,H coupling constant appears anomalously large (thus in Vi_2Tl : $J_{Tl,H} \sim 200 \times J_{H,H}$), this is probably connected with the geometry of the system and will be discussed later. All of the Tl,H coupling constants have the same positive sign

which is consistent with the positive H,H couplings observed in vinyl compounds where X is a more electropositive element. Similar large positive values for the geminal M,H coupling constants appear in Vi_2Hg and Vi_4Sn, these are shown in Table 5(b).

In the H,H coupling constants of various methyl substituted vinyls it is found that (49, 10),

$J_{H,H(CH_3 cis)} = -1.7$ to -1.9 c/sec.; $J_{H,H(CH_3 trans)} = -1.2$ to -1.3 c/sec.

whilst $J_{H,H(CH_3\ vicinal)} = +6.0$ c/sec. $\left\{ \equiv \overset{\backslash}{\underset{/}{C}} = C \begin{matrix} H \\ \diagup \\ \diagdown \\ CH_3 \end{matrix} \right\} J$

Electronegative substituents decrease these coupling constants slightly. Again, if the Tl,H couplings (shown in Table 9(a)) are divided by ~ 55 (as in ϕ_2Tl^+), they give values which vary in magnitude and sign in the same manner as the H,H couplings. Whereas the cis and trans $Tl,H(CH_3)$ couplings have negative signs, the Tl,H couplings in the vinyl thalliums are positive. (It was not possible to test the sign of the $Tl,H(CH_3)$ vicinal coupling, but this is probably positive.) The change of sign on substituting a vinyl proton by a methyl group is required by Karplus's theory (41) for the π -contribution to the H,H coupling constants. Although the Tl,H couplings undoubtedly involve large π -contributions these are probably of similar magnitude to the σ -contributions over four bonds. It is also noticeable that the $Tl,H(CH_3)$ vicinal coupling in $(CH_3CH = C.CH_3)_2Tl^+$ is much less than the β -coupling in Et_2Tl^+ (Table 6(a)), and that, whereas in the Tl,Hgem couplings with the vinyls there is little correspondence with the H,H gem couplings; in this case the ratio of ~ 55 again holds.

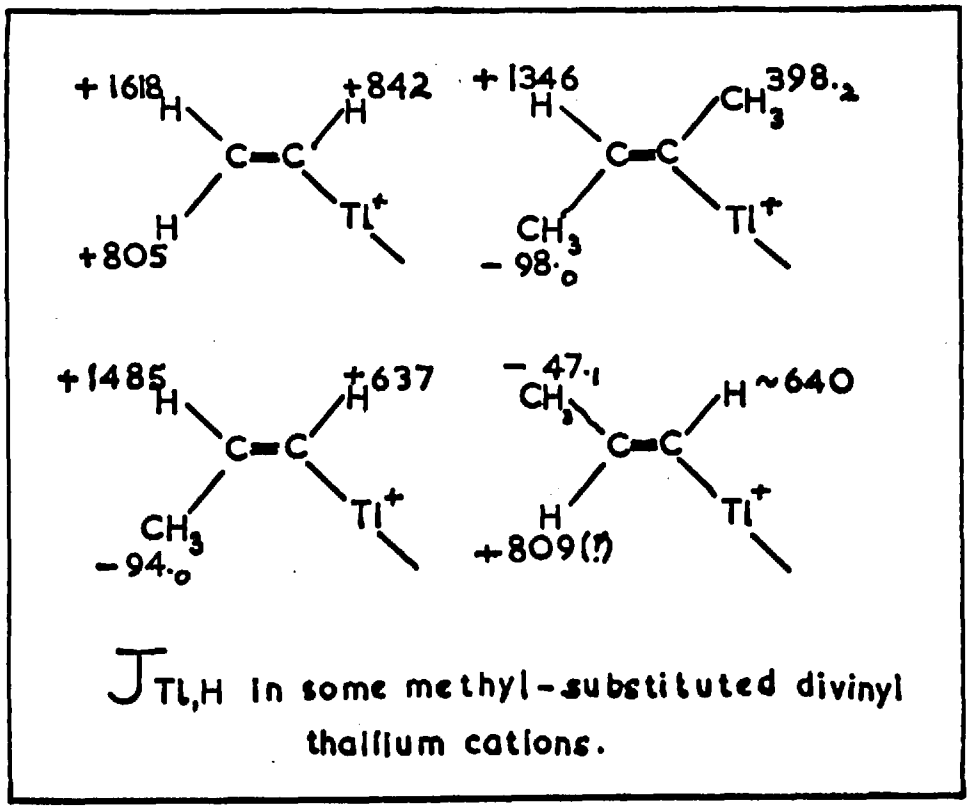
The small decreases found for the Tl,H couplings as a consequence

of the substitution of methyl groups for protons, may be a result of the different effective electronegativities of these groups, of changes in bond angles, or of changes in bond distances. The Tl,H coupling constants are evidently highly sensitive to all of these factors.

The dependence of the Tl,H coupling constants on the electronegativity of the attached group is illustrated by the spectrum of trans-$(CHCl = CH)_2Tl^+$ (Fig.12). The substitution of another electronegative group (such as a chlorine) in vinyl compounds, causes a decrease in the H,H coupling constants; this is seen from equations A and B. It was not possible to assign coupling constants from the spectrum of trans$(CHCl = CH)_2Tl^+$; however they are either $486._3$ and $476._7$ c/sec, or $510._5$ and $452._5$ c/sec. for either the geminal or the cis Tl,H coupling constants. The spectrum shows immediately that both of these couplings have the same sign. Whichever of the values are chosen it is noticeable that the Tl,H(cis) coupling is about 60 times the H,H(cis)coupling (cf. $J_{H,H(cis)} = + 7.3$ c/sec. in vinyl chloride). The cis and geminal Tl,H couplings have about the same relative magnitudes as in the unsubstituted vinyl thalliums. The chlorine decreases both of these couplings by about the same amount, and the Tl,H (gem) coupling again appears anomalously large in comparison to the H,H(gem) coupling. A comparable effect is observable for the couplings in trans$(CHCl = CH)_2Hg$ and trans-$(CHCl = CH)HgCl$ (Fig.12, Table 11.)

The H,H coupling constants for the vinyl thalliums are shown in Table 9(c).

TABLE 9a.



$J_{Tl,H}$ in some methyl-substituted divinyl thallium cations.

Table 9 (b). H,H coupling constants in the vinyl thalliums.

Compound.	J_{Cis} c/sec.	J_{Trans} c/sec.	J_{Gem} c/sec.	$\sum J$.	Electro-negativity (21)
$(Vi,Me)_3Tl$	12.8 ± 0.2	20.0 ± 0.2	4.3 ± 0.2	37.1	2.0
Vi_2Tl^+	11.6 ± 0.5	19.4 ± 0.5	< 1	31	2.4
$ViTl^{2+}$	9.0 "	17.0 "	< 1	26	2.8

In the propenyl thalliums $J_{H,H(CH_3Gem)} = 6.0 \pm 0.3$ c/sec.

For both the chloro-vinyl mercury and thallium compounds,

$$J_{H,H\ trans} = 15.0 \pm 0.5 \text{ c/sec.}$$

Alkyl thalliums. (Tables 6 & 10. Figs. 3,10 & 11.)

The vicinal H,H couplings in substituted hydrocarbons are normally $\sim$ + 8 c/sec; they are very dependent upon the conformation of the alkyl chain. For substituted ethyl compounds CH_3CH_2X, the vicinal H,H coupling depends slightly on the electronegativity of X, i.e.

$$J_{vic} = + 7.9 - 0.7\Delta E \quad (\Delta E = E_X - E_H),$$

(42,60). Compared to these couplings, the Tl,H(β CH) couplings in the dialkyl thallium cations (Table 10), are $\sim$ 65 times greater; this ratio compares favourably with those previously obtained for the diphenyl and divinyl thallium cations.

In substituted methanes the geminal H,H couplings fall between -9.5 and - 15.5 c/sec. (42) (in methane $J_{H,H} = - 12.4$ c/sec.); thus the geminal Tl,H_α couplings in the dialkyl thallium cations are $\sim$25 times greater than the corresponding geminal H,H couplings. Both have negative signs. The magnitude of the geminal Tl,H_α coupling appears much smaller (less negative), than would be expected from the ratios obtained in the other comparisons between the Tl,H and H,H couplings. This will be commented on later.

The Tl,H couplings shown in Table 10, although variable, do follow some general patterns. Thus the α-CH coupling decreases in the series Me_2Tl^+, Et_2Tl^+, $i\text{-}Pr_2Tl^+$, with increasing methyl-substitution on the α-position. This change may be connected with changes in the Tl-C-H bond angle, but it may also be a result of hyperconjugation; the substitution of a methyl group for a proton would decrease the amount of hyperconjugation, which could change the contribution to the coupling from

valonce bond structures involving a direct Tl-H bond.

In the series Et_2Tl^+, $n\text{-}Pr_2Tl^+$, $i\text{-}Bu_2Tl^+$ and $n\text{-}Bu_2Tl^+$ the $\alpha\text{-}CH_2$ coupling remains approximately constant; since the environment of the $\alpha\text{-}CH_2$ group does not change very much, this situation is not unexpected. The small differences which are observed in the $\alpha\text{-}CH_2$ coupling can probably be attributed to small conformational changes in the hydrocarbon chains.

At the β-carbon, the coupling to a $\beta\text{-}CH_3$ is much greater than to a $\beta\text{-}CH_2$, but increases again for a $\beta\text{-}CH$ (cf. $i\text{-}Bu_2Tl^+$); again, these variations could reflect the conformational differences of the alkyl chains.

In ethane, the vicinal H,H coupling (8.0 c/sec. (38)), is the mean of the trans and gauche couplings $(\frac{1}{3}J_t + \frac{2}{3}J_g)$. The ratio $J_t/J_g \doteq 5$ (61), is in good agreement with the theoretical value of 5.4 (41). The spectrum of the $(cyclopentyl)_2Tl^+$ cation provides a nice illustration of the effect of the stereochemistry of the alkyl chain on the couplings. Thus the $\alpha\text{-}CH$ and one of each of the $\beta\text{-}CH_2$ protons (assigned to $\beta\text{-}CH$(cis) by analogy with the H,H couplings) have Tl,H couplings of roughly the same magnitudes, whilst the $\beta\text{-}CH$(trans) protons show a greater Tl,H coupling than either of these. This assignment is a tentative one and is based on the relative areas of the individual signals (shown in Fig.11 G). A further point of interest are the broad featureless lines, which show no fine structure from the H,H coupling. This effect is probably due to a rapid intramolecular interchange between two conformational isomers (cf. the rapid ring

Table 10.

Tl,H coupling constants in various dialkyl thallium cations.

Compound	$J_{\alpha\text{-CH}}$ c/sec.	$J_{\beta\text{-CH}}$ c/sec.	$J_{\gamma\text{-CH}}$ c/sec.
Me_2Tl^+	$402._7$	-	-
Et_2Tl^+	$-340._4$	$+628._0$	-
$i\text{-}Pr_2Tl^+$	$258._9$	$574._0$	-
$n\text{-}Pr_2Tl^+$	$-340._7$	$+468._9$	$+20._5$
$i\text{-}Bu_2Tl^+$	$-356._0$	$+493._7$	$+16._4$
$n\text{-}Bu_2Tl^+$	$319._6$	$451._8$	?
$(Et\text{-}Tl\text{-}Me)^+$			
Me	$359._0$	-	-
Et	$399._3$	$679._5$	-
$(cyclopentyl)_2Tl^+$	214	214/466	?

Table 11.

Hg^{199},H coupling constants in various organo-mercury compounds.

R	R_2Hg c/sec.	RHg^+ c/sec.
Methyl	$102._5$	$260._2$
Ethyl CH_2	$87._6$	$213._5$
Ethyl CH_3	$115._2$	$296._9$
ClCH = CH - cis or trans.	$55._0$	$122._3$
ClCH = CH - cis or trans.	$89._8$	$162._2$

Tolyl mercuric acetates:		
	$J_{Hg,H(CH_3\ ortho)}$	$21._0$ c/sec.
	$J_{Hg,H(CH_3\ meta)}$	"
	$J_{Hg,H(CH_3\ para)}$	$12._5$ "

inversion of the 'chair' conformation of cyclohexane (62)). The spectrum of $(cyclopentyl)_2Tl^+$ did not change on lowering the temperature of the sample to $\sim 0^\circ$.

There are a few instances of H,H coupling over four bonds in substituted hydrocarbons (42) ; these are usually < 0.8 c/sec., and may have either a positive or a negative sign. Such couplings have been found to be very stereospecific, and their values are greatest when all five atoms are co-planar $H\diagdown C - C - C\diagup H$ (63). The small Tl,H(γ-CH_3) couplings in the $n\text{-}Pr_2Tl^+$ and the $i\text{-}Bu_2Tl^+$ cations are consistent with the greater magnitudes of the Tl,H couplings when compared to the H,H couplings. Brownstein (64) has found couplings of similar magnitudes, $J_{Hg^{199},H(\gamma\text{-}CH)}$ in various compounds of the type $CH_3OR.HgX$, where R is an organic radical and X a halide or acetate. The Hg,H(γ-CH) couplings were usually ~ 20 c/sec. and very dependent upon R. Brownstein concluded that the differences were due to different preferred conformations.

The Mixed Trialkyl Thalliums. (Figs.3 & 4, Tables 3 & 4.)

In these alkyls the regular changes observed in the Tl,H couplings are probably due to differences in the electronegativities of the attached groups. The more electronegative group will attract more p-character into its Tl-C bond, so lowering its own coupling(s) (a feature consistent with a predominant contribution from the Fermi contact interaction). At the same time there will be a decrease in the relative p-character, and an increase in the relative s-character, in the Tl-C bond of the other less electronegative group, which will increase its' coupling(s). A similar effect is observable for the couplings for the

$(Me\text{-}Tl\text{-}Et)^+$ cation. Malinowski(65) has shown that to a good approximation the C^{13},H couplings in various substituted methanes CHXYZ, are an additive property of the substituent, this may be written (37),

$$J_{CH(CHXYZ)} = J_{CH(CH_4)} + \delta_X + \delta_Y + \delta_Z$$

where $$\delta_X = J_{CH(CH_3X)} - J_{CH(CH_4)}.$$

thus each substituent X contributes a characteristic term δ_X to $J_{CH(CHXYZ)}$ which is independent of the other substituents. Likewise Y and Z. Gutowsky and Juan (37) found that this relation can be derived by assuming that the substituent changes the hybridisation of the carbon 2s orbital, so changing the Fermi contact contribution.

The Tl,H(methyl) couplings are consistent with an order of effective electronegativity of

$$CH_2 = CH- \; > \; CH_3- \; > \; C_2H_5- \; .$$

This is the order we should expect from the relative inductive effects of these groups observed in organic compounds. Some of the changes in the Tl,H couplings show a roughly linear substituent effect; however the changes in the ethyl group Tl,H(CH_3) couplings on substituting methyl groups are definitely non-linear. Gutowsky and Juan ascribe deviations from the additivity relation to the inductive effect of the electronegative substituents on an easily polarisable atom. Non-additive substituent effects in C^{13},H 'directly bonded' couplings have recently been noted by Muller and Rose (66).

The Tl,H coupling for solutions of Me_3Tl in trimethylamine and dimethyl ether is greater than that for solutions of Me_3Tl in dichloromethane or toluene (Tables 2 and 6); this is unexpected. The

The coordination of a trimethylamine molecule in $Me_3\overset{+}{N} \rightarrow \overset{-}{T}lMe_3$, both decreases the amount of s-character in the Tl-C bond ($sp^2 \rightarrow sp^3$) and increases the negative charge on the thallium; for both of these reasons we expect the Tl,H coupling to decrease. It is possible that this decrease is cancelled out by another factor, for instance a decrease in the Tl-C-H bond angle might increase the Tl,H coupling (45).

Scholium.

The resemblances found between the Tl,H and the H,H coupling constants are good evidence that the coupling mechanisms for both of these are similar. Thus the Tl,H couplings like the H,H couplings are probably dominated by the Fermi contact interaction. The contributions from $)H_1$ and $)H_2$ are probably also increased in proportion to the greater magnitude of the Tl,H couplings. A predominantly Fermi contact interaction mechanism is supported by Klose's calculations (45), and by the agreement between the experimental and the theoretical ratios for the Tl,H coupling constants in the series $R_3Tl : R_2Tl^+ : RTl^{2+}$.

However, when comparing the Tl,H and H,H coupling constants the geminal Tl,H coupling constants have a different, apparently anomalous, behaviour. The variation in the geminal Tl,H coupling constant being between -350 c/sec. in R_2Tl^+, and +840 c/sec. in Vi_2Tl^+; compared with the geminal H,H coupling constants of -12.4 c/sec. in methane, and +2.5 c/sec. in ethylene. Thus although the Tl,H and H,H coupling constants vary in the same way, the variation is in a more positive sense for the Tl,H coupling constants. If the total

variations of the Tl,H and H,H coupling constants are compared, ($\sim$1200 c/sec. in $J_{Tl,H}$: $\sim$ 15 c/sec. in $J_{H,H}$ (methane to ethylene)), the Tl,H coupling constant variations are seen to be larger by about the expected factor (i.e. $J_{Tl,H} \sim 75 \times J_{H,H}$).

In his calculation, Klose (45), finds that in ethyl compounds C_2H_5X, for light isotopes X with a positive sign relation between the X X,H(α-CH) and the X,H(β-CH) coupling constants, the XH(α-CH) coupling constant decreases with increasing $\widehat{XCH}$, goes through zero and takes on increasing negative values. However for heavy isotopes, in which the X,H(α-CH) coupling constant is negative, the XH(α-CH) coupling constant increases with increasing $\widehat{XCH}$ and goes through zero with increasing positive values. A large positive increase is observed for the geminal Tl,H coupling constants when the bond angle, $\widehat{TlCH}$, is increased (cf. in Et_2Tl^+, $\widehat{TlCH} \sim 109^\circ$ (tetrahedral), and in Vi_2Tl^+, $\widehat{TlCH} \sim 120^\circ$ (trigonal)). However, Klose's predictions are at variance with the experimental values for the H,H coupling constants where the same increase on increasing the bond angle $\widehat{HCH}$, occurs. Thus the agreement between Klose's calculations, and the author's experimental findings may be fortuitous.

Further evidence that heavy-metal,proton coupling constants are dominated by the Fermi contact interaction could be obtained by studying the Hg^{199},H and Pb^{207},H coupling constants. Some Hg,H coupling constants where they are available, have already been compared with the Tl,H coupling constants, and these so far seem to follow the same type of pattern. The ratio between the coupling constants in

RHg^+ and R_2Hg compounds (Table 11), is about the same as the ratio between the coupling constants in RTl^{2+} and R_2Tl^+ (using $Z_c = 5$ for Hg in HgX_2, the calculated ratio between the couplings in R_2Hg and RHg^+ is 1:2.4). Also in the tolyl mercuric acetates, the coupling follows the same pattern as for the tolyl thalliums. The greater magnitude of the Tl,H couplings as compared to the Hg,H couplings, is mainly accounted for by the larger magnetic moment of the thallium (Table 5(a)).

Table 5(a) indicates that the similarities between the X,H and the H,H coupling constants become less as we go across the Periodic Table. This would parallel an increase in the importance of p- and d-orbitals to the bonding, so making the contributions from $\mathcal{H}_1$ and $\mathcal{H}_2$ relatively more important (cf. the coupling constants for Et_3P and EtF).

FIG 5

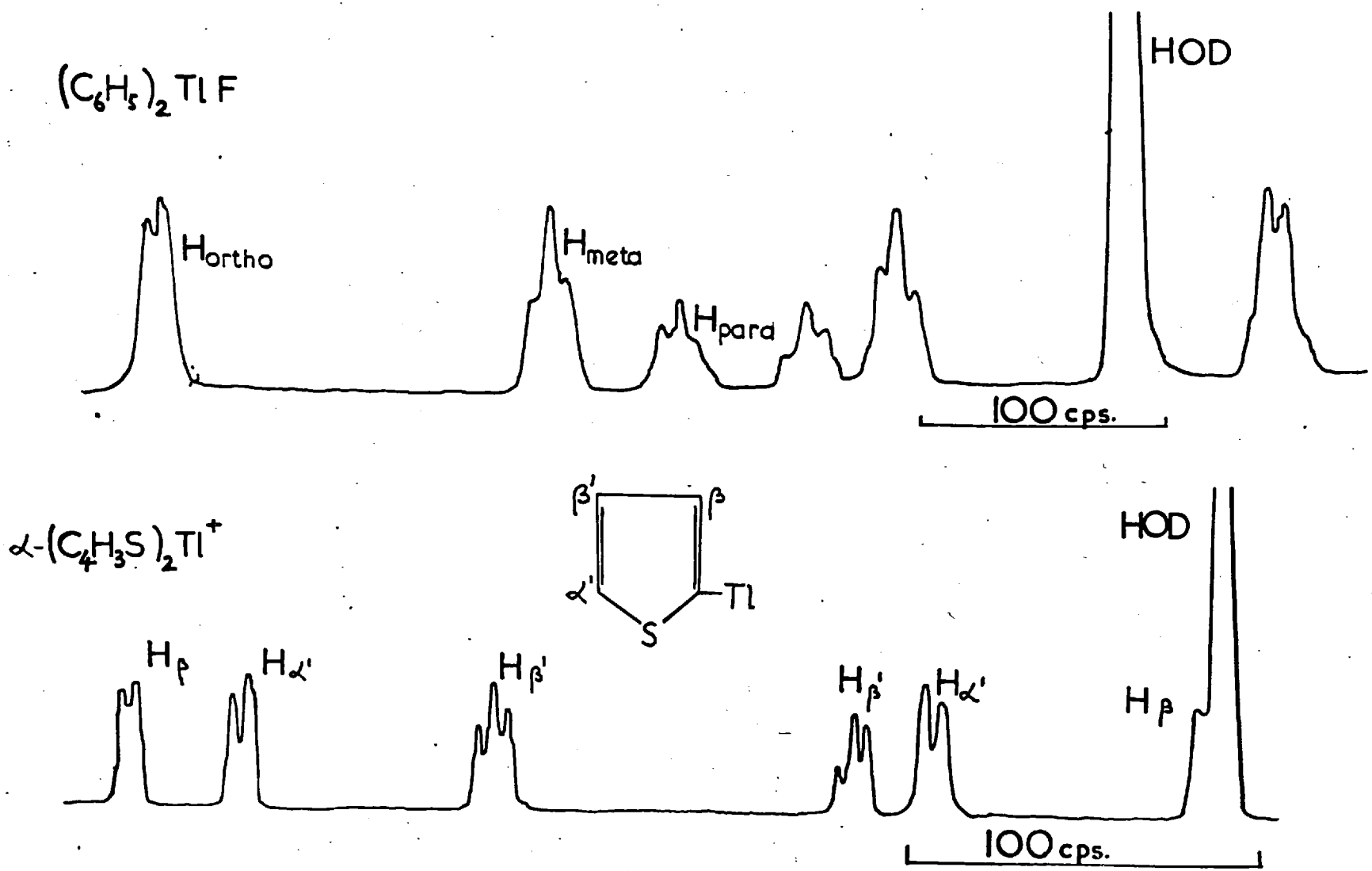

$(C_6H_5)_2TlF$
HOD
H_{ortho}
H_{meta}
H_{para}
100 cps.
α-$(C_4H_3S)_2Tl^+$
β'
β
α'
Tl
S
HOD
H_β
$H_{\alpha'}$
$H_{\beta'}$
$H_{\beta'}$
$H_{\alpha'}$
H_β
100 cps.

FIG 6

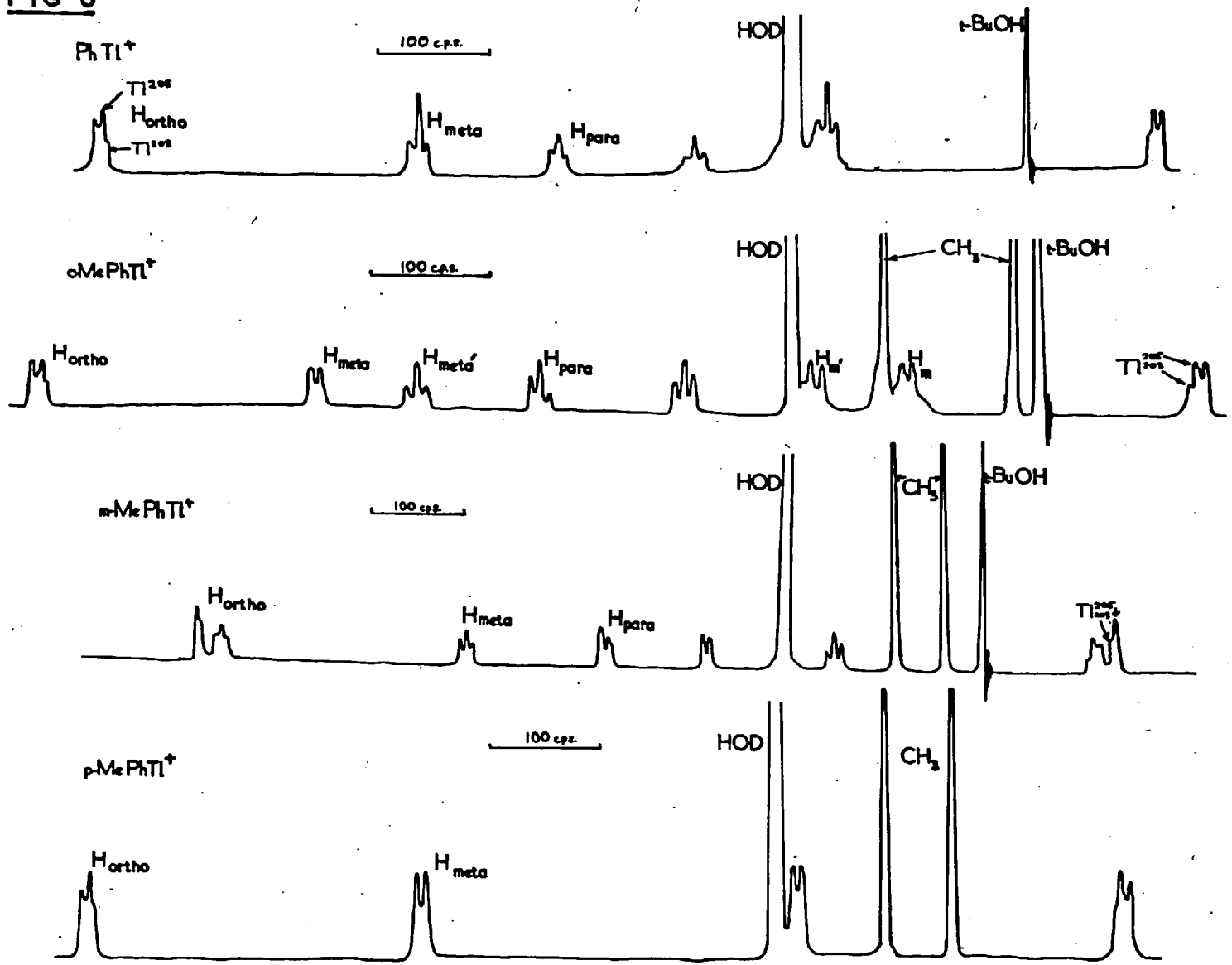
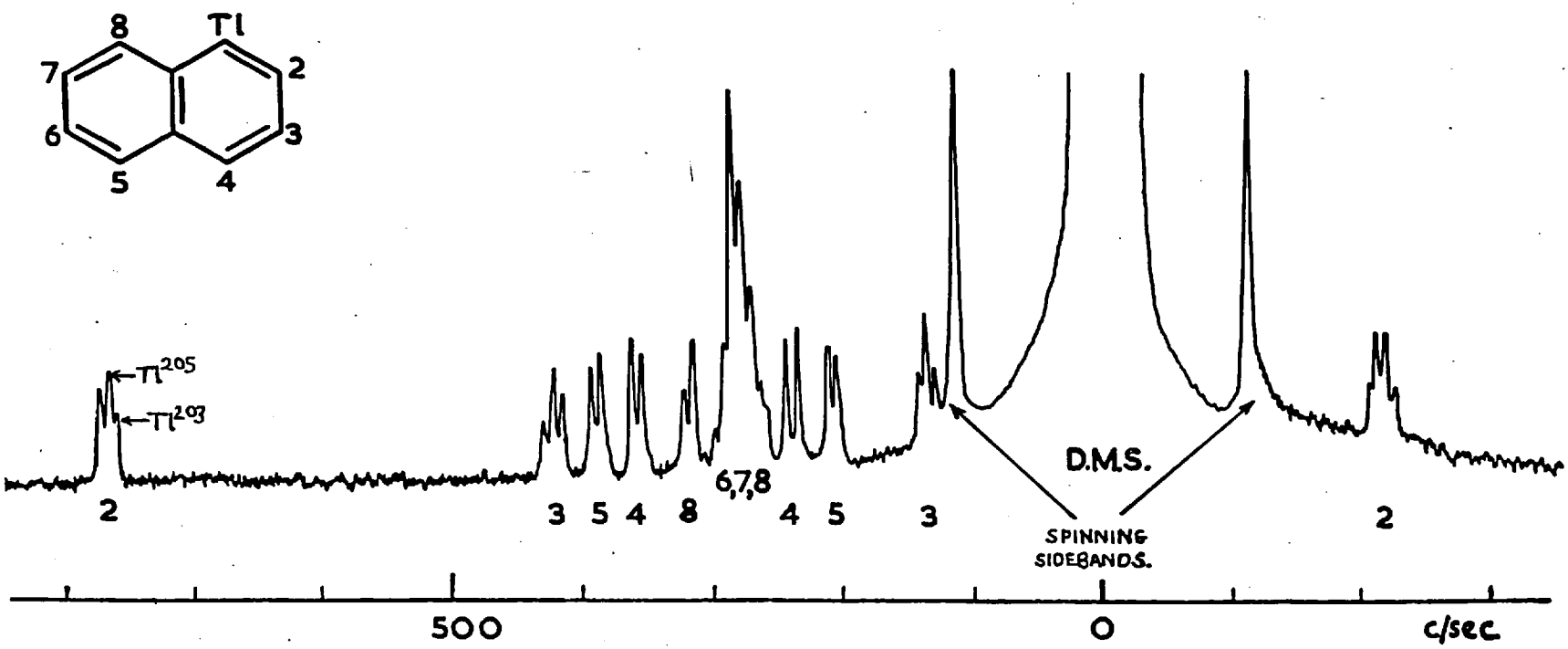

PhTl+
100 c.p.s.
Tl2ort
Hortho
Tl2ort
Hmeta
Hpara
HOD
t-BuOH
oMePhTl+
100 c.p.s.
HOD
CH3
t-BuOH
Hortho
Hmeta
Hmeta'
Hpara
Hm'
Hm
Tl2ort 2ort
m-MePhTl+
100 c.p.s.
HOD
CH3
t-BuOH
Hortho
Hmeta
Hpara
Tl2ort 2ort
p-MePhTl+
100 c.p.s.
HOD
CH3
Hortho
Hmeta

FIG 7. 1-Napthyl Thallium Dichloride in Dimethyl Sulphoxide.



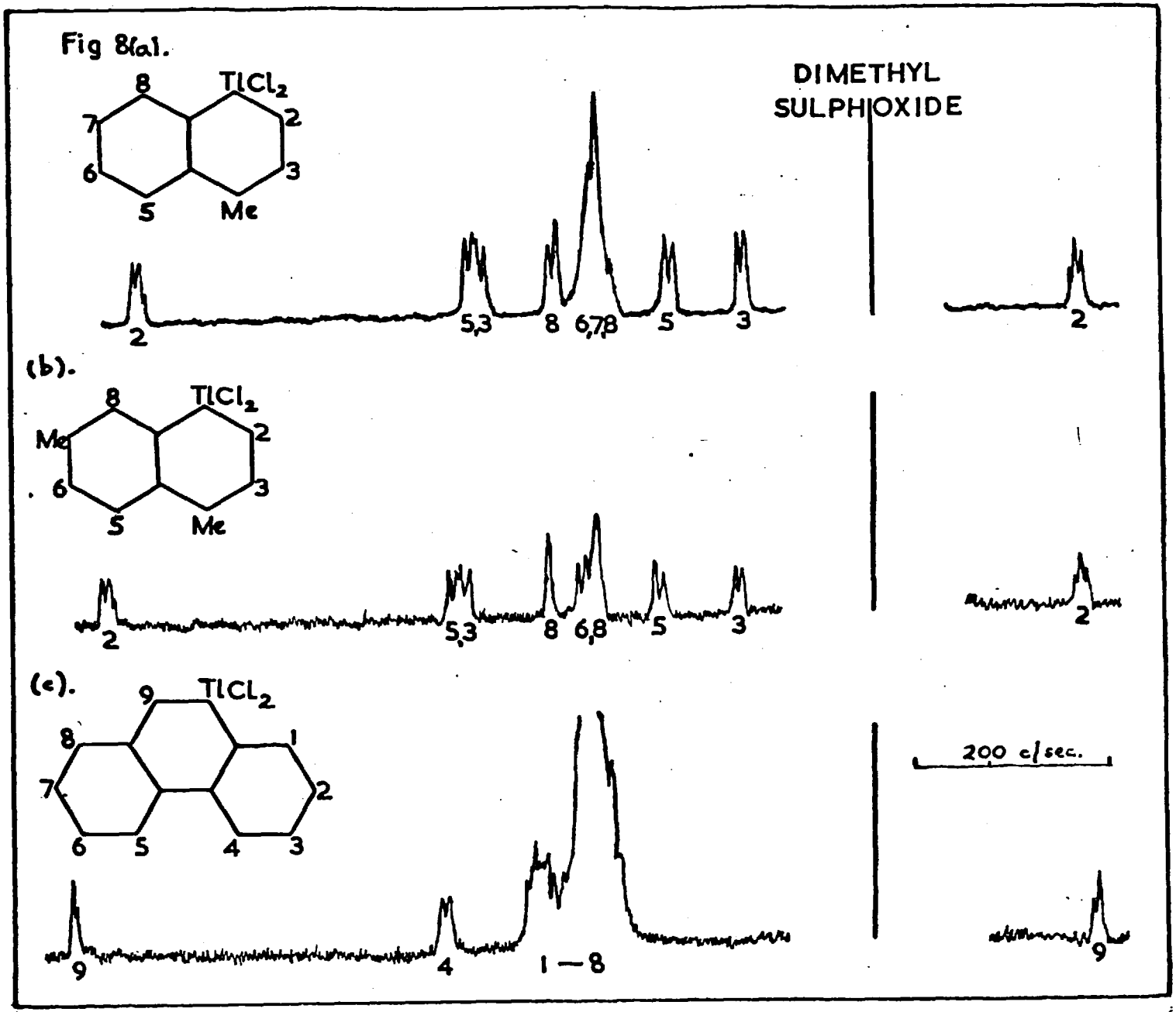

Fig 8(a).
DIMETHYL SULPHOXIDE
8
TlCl2
7
2
6
3
5
Me
2
5,3
8
6,7,8
5
3
2
(b).
8
TlCl2
Me
2
6
3
5
Me
2
5,3
8
6,8
5
3
2
(c).
9
TlCl2
8
1
7
2
6
5
4
3
200 c/sec.
9
4
1—8
9

FIG 9. VINYL THALLIUMS.

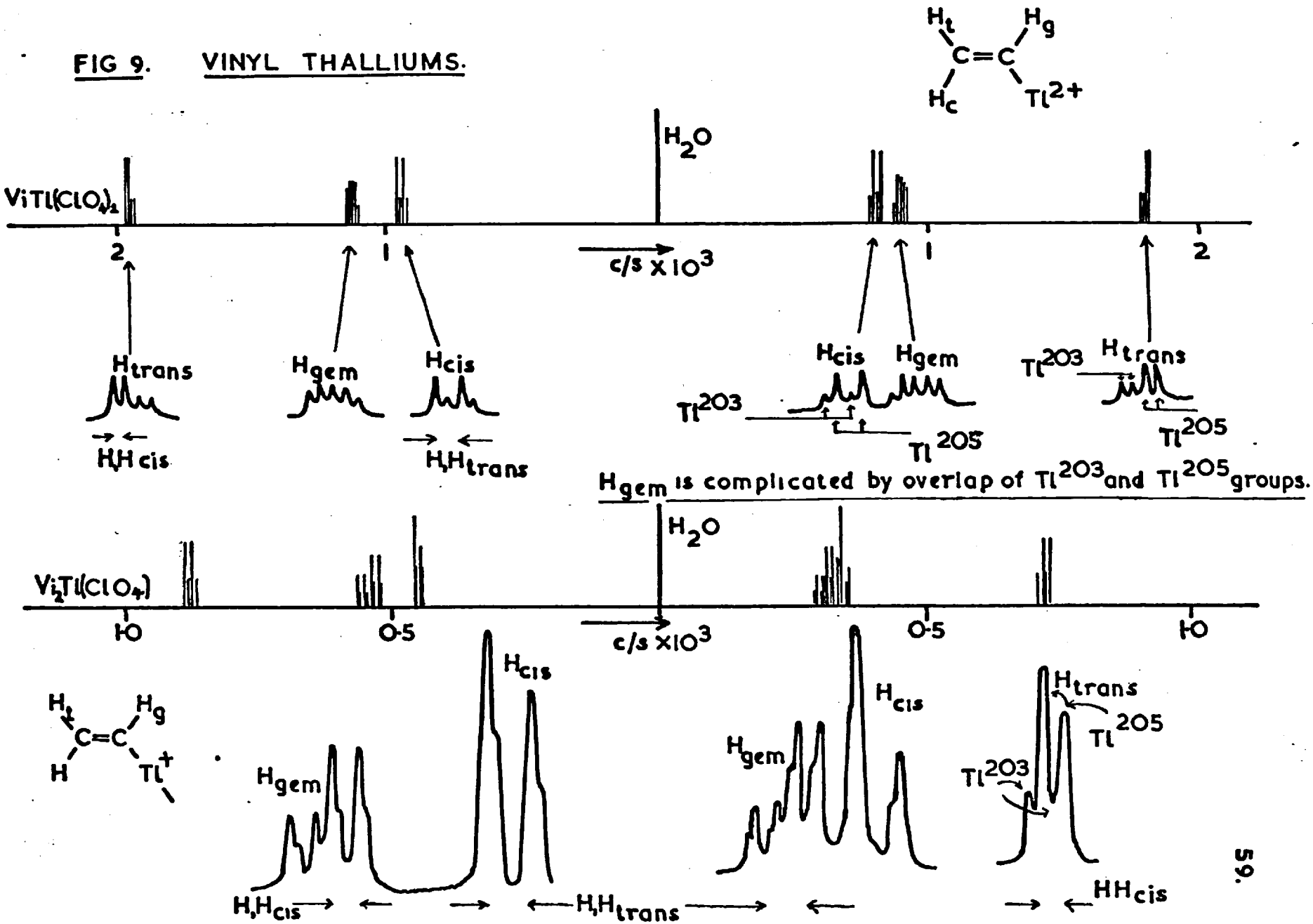


FIG 10

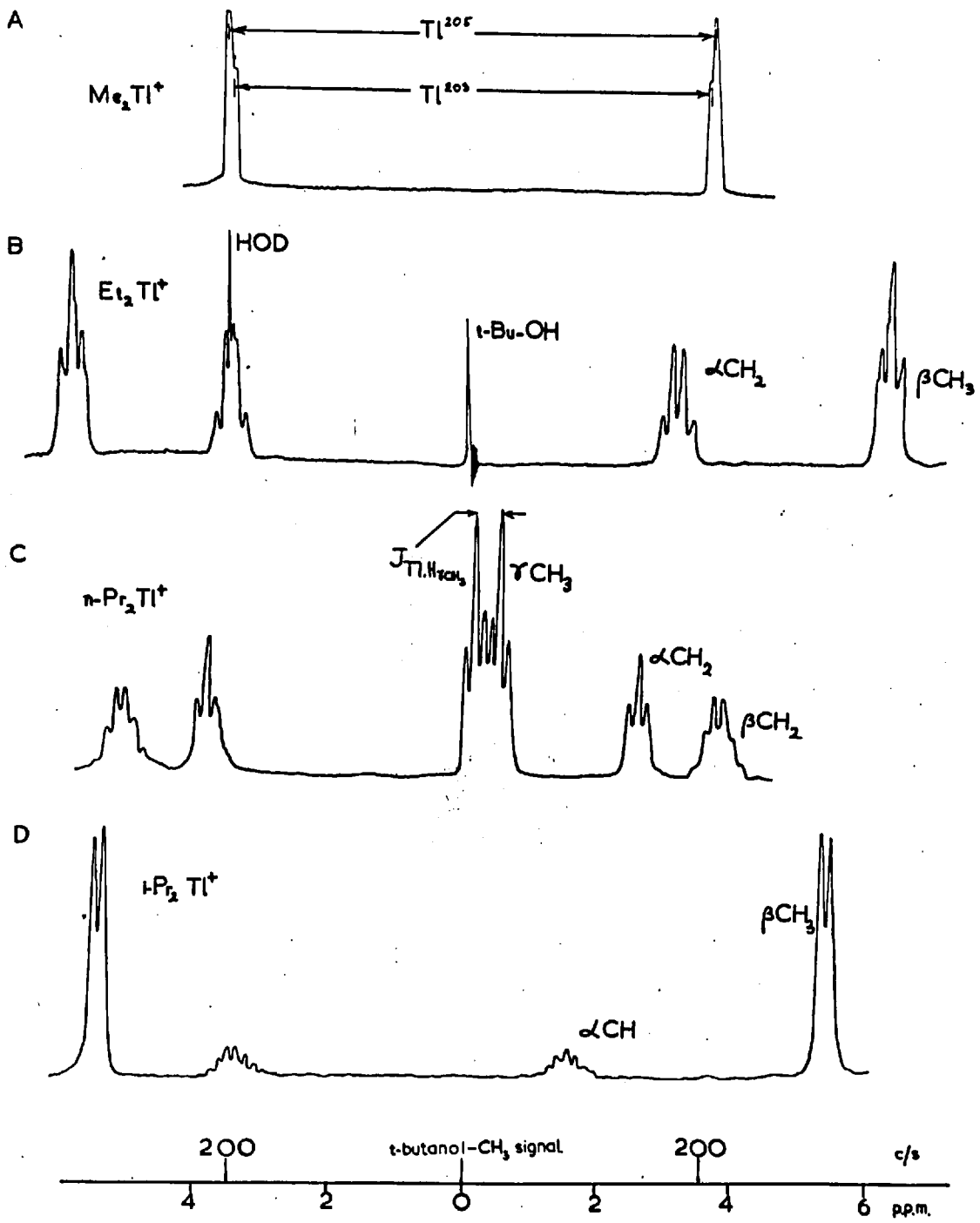

A
Me_2Tl^+
Tl^{205}
Tl^{203}
B
Et_2Tl^+
HOD
t-Bu-OH
αCH_2
βCH_3
C
n-Pr_2Tl^+
$J_{Tl,H_{\gamma CH_3}}$
γCH_3
αCH_2
βCH_2
D
i-Pr_2 Tl^+
βCH_3
αCH
200
t-butanol-CH_3 signal
200
c/s
4
2
0
2
4
6
p.p.m.

FIG II.

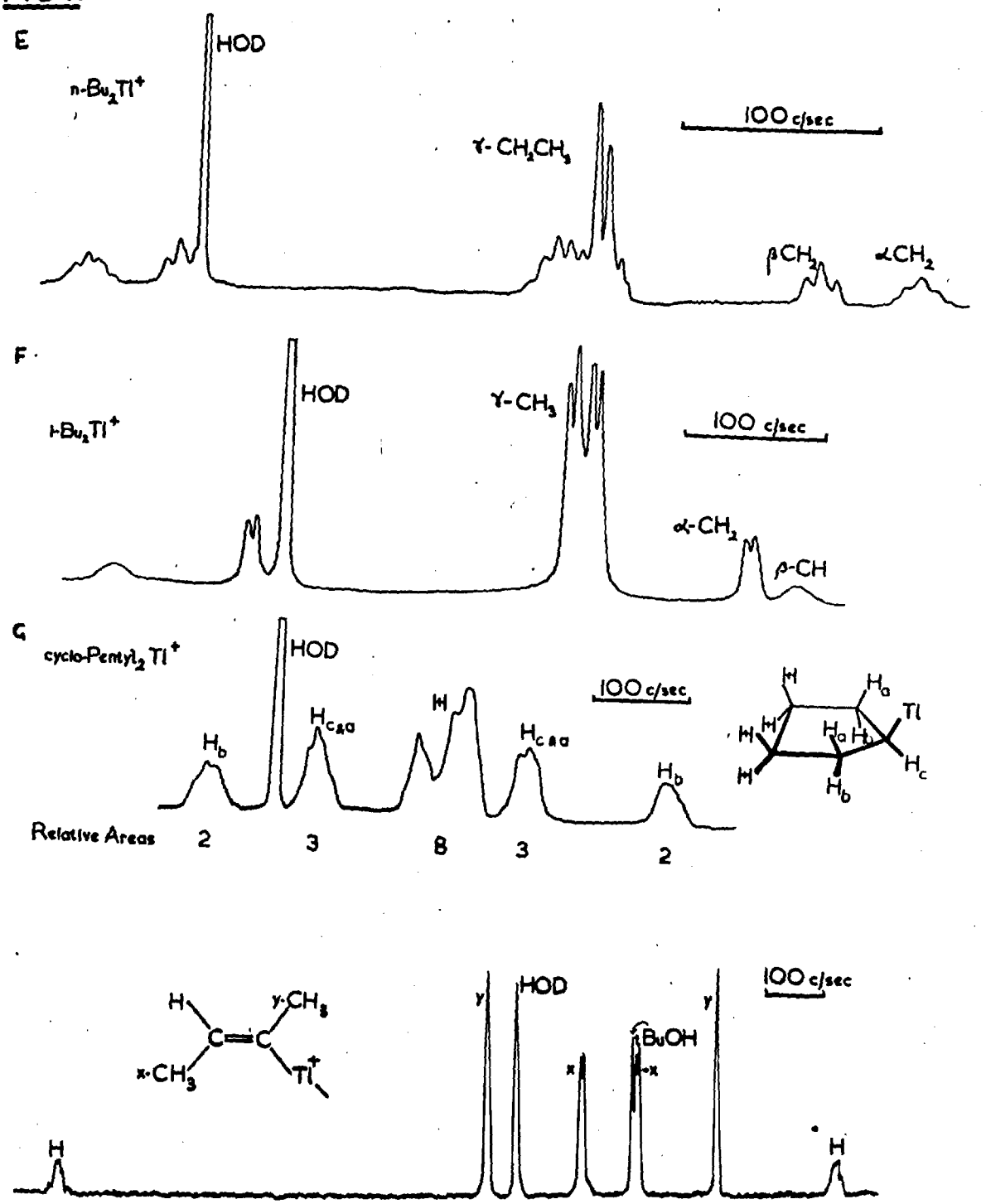
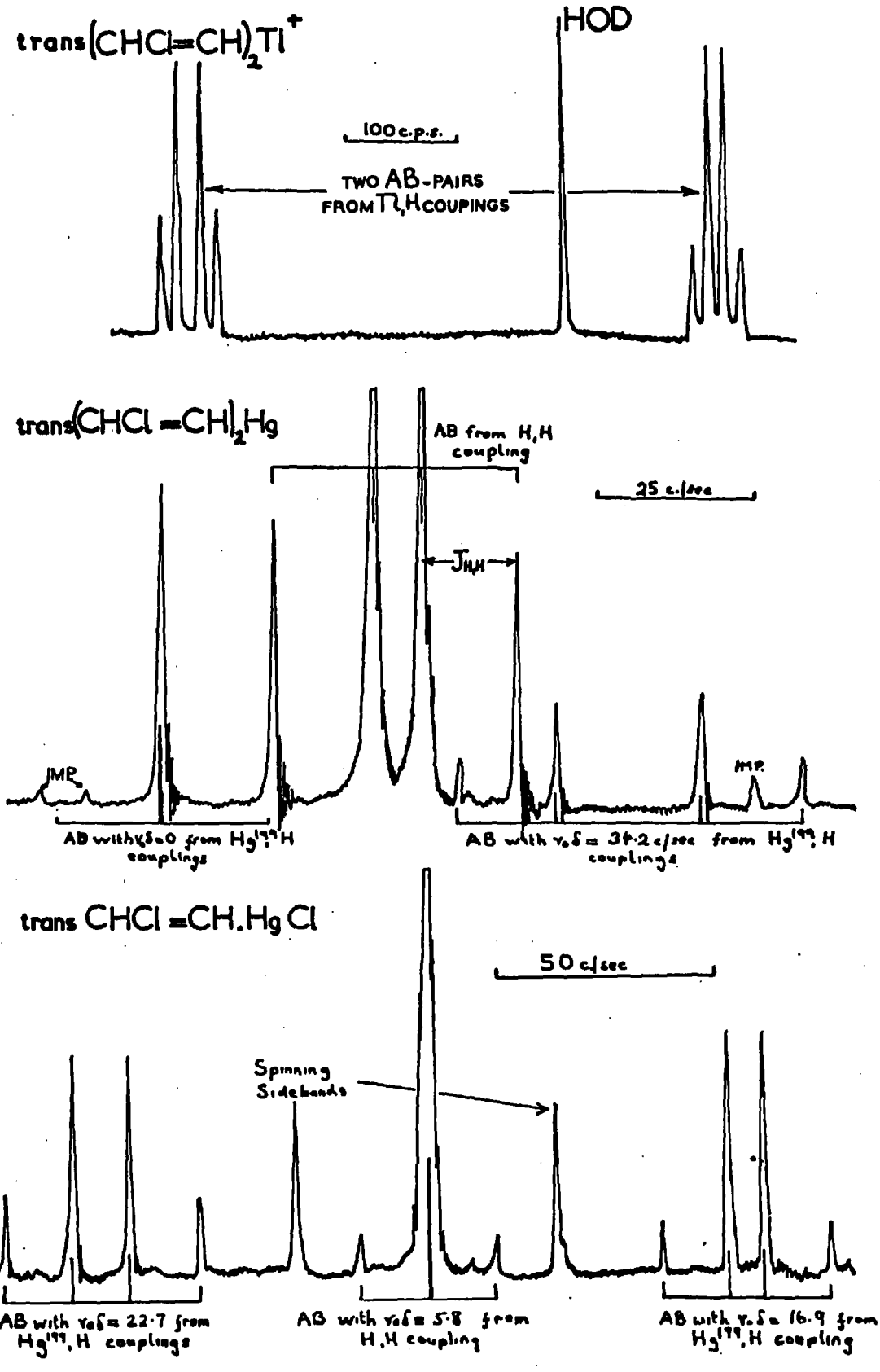

E
n-Bu₂Tl⁺
HOD
γ-CH₂CH₃
100 c/sec
βCH₂
αCH₂
F
i-Bu₂Tl⁺
HOD
γ-CH₃
100 c/sec
α-CH₂
β-CH
G
cyclo-Pentyl₂ Tl⁺
HOD
100 c/sec
Hb
Hc,a
H
Hc,a
Hb
Relative Areas
2
3
8
3
2
Ha
Tl
Hc
H
Hb
H
H
H

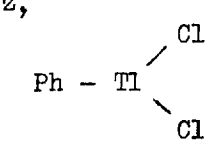
FIG 12


trans (CHCl=CH)2Tl+
HOD
100 c.p.s.
TWO AB-PAIRS FROM Tl,H COUPINGS
trans (CHCl=CH)2Hg
AB from H,H coupling
25 c./sec
JH,H
IMP.
IMP.
AB with γδ=0 from Hg199,H couplings
AB with γδ = 34·2 c/sec from Hg199,H couplings
trans CHCl=CH.HgCl
50 c/sec
Spinning Sidebands
AB with γδ= 22·7 from Hg199,H couplings
AB with γδ= 5·8 from H,H coupling
AB with γδ= 16·9 from Hg199,H coupling

CHAPTER IV.

The Constitution of monophenyl and monovinyl thallium dichloride.

The far infra red spectrum of a solid mull of phenyl thallium dichloride shows one narrow absorption, which is assigned to a Tl-Cl stretching mode (ν = 313 cm^{-1}; in $TlCl_4^-$ the assymetric Tl-Cl stretch occurs at $\sim$ 300 cm^{-1} (67)). The spectrum also shows an unspecified phenyl peak at 229 cm^{-1}. This indicates that in the solid state this compound exists as $(Ph\text{-}Tl\text{-}Cl)^+Cl^-$, since if it had a trigonal form viz,



two absorptions, corresponding to a symmetric and an antisymmetric Tl-Cl stretching mode would be expected.

Phenyl thallium dichloride is slightly soluble ($\sim$ 0.5%) in water, and very soluble in dimethyl sulphoxide. Conductivity measurements of the ion in water indicated that it is almost completely dissociated to $PhTl^{2+}$ and 2 Cl^- at M/1000 (Λ^{25° = 218 $ohms^{-1}cm.^2$), but that with lower concentrations there is considerable hydrolysis. Λ^{25° decreases slightly for solutions stronger than M/1000 indicating the presence of some $(Ph\text{-}Tl\text{-}Cl)^-$. A study of $PhTlSO_4$ showed that there is very considerable hydrolysis; $PhTl(NO_3)_2$ disproportionated very rapidly to give the Ph_2Tl^+ ion.

The coupling constants for solutions of $PhTlCl_2$ in dimethyl sulphoxide, and $PhTl(ClO_4)_2$ in water are compared in Table 12. They are concentration independent for the fairly concentrated solutions studied ($\sim$ 10%). In water, the Tl,H coupling constants for the $PhTl^{2+}$

cation were not affected by the presence of perchloric acid. The differences between the Tl,H coupling constants for these compounds are probably attributable to the different states of the ions in solution; the coordination of a negative chloride ion will change the hybridisation of the thallium and decrease its effective nuclear charge so lowering the coupling constants.

Similar changes are observed for the coupling constants of $ViTl(ClO_4)_2$ and $ViTlBr_2$ in dimethyl sulphoxide solution: ($ViTl(ClO_4)_2$, $J_{Tl^{205},H(trans)}$= 3838 c/sec.; $ViTlBr_2$, $J_{Tl^{205},H(trans)}$=3159 c/sec.). The larger Tl,H(trans) coupling constant of $ViTl(ClO_4)_2$ in dimethyl sulphoxide solution as compared with the coupling constant for this compound in aquous solution (Table 6(a)) may be due to the greater polarity of the dimethyl sulphoxide molecule, and hence the greater effective electronegativity of the oxygen in dimethyl sulphoxide as compared to the oxygen in water.

The variations in the Tl,H coupling constants are similar to the variations observed in the $Hg,H(CH_3)$ coupling constants in CH_3HgX (68) cf. $X = ClO_4^-$, J=260.$_2$ c/sec.

$X = Cl^-$, J=202.$_4$ " .

These changes may be interpreted in terms of the different acid strengths of X. The more electronegative that X is, the higher the coupling constant.(69).

Table 12.

Compound	Solution	$J_{Tl,H(ortho)}$	$J_{Tl,H(meta)}$	$J_{Tl,H(para)}$.
$PhTlCl_2$	D.M.S.	875	334	115
$PhTl(ClO_4)_2$	D_2O	948	365	123

CHAPTER V.

Experimental.

As most of these preparations involve standard procedures they will only be outlined. However, new preparations are given in detail, and some reactions which failed to give the required compounds are briefly described. The methods of handling the reactive and unstable trialkyls are described.

* * *

Thallic bromide was prepared by reacting bromine with thallous bromide in tetrahydrofuran.

Thallic chloride could not be prepared by passing chlorine through a suspension of thallous chloride in tetrahydrofuran or ether, due to extensive chlorination of the solvent. It was prepared by passing chlorine into an aquous suspension of thallous chloride, afterwards removing the water in a vacuum desiccator over concentrated sulphuric acid.

Dialkyl and Diaryl thallium bromides (6) were prepared by reacting thallic bromide with the Grignard reagent (a 10% excess) in diethyl ether. The flask was cooled in an ice/salt bath, and the Grignard reagent was added to the thallic solution over a period of ~ I hour. The product was hydrolysed with I% ammonium bromide solution, and the solid was filtered and extracted with hot 1/1 aquous ammonia or warm pyridine. On cooling, beautiful white glistening crystals were deposited.

$$TlBr_3 + 2RMgBr = R_2TlBr + 2MgBr_2$$

Divinyl thallium Bromide was prepared by reacting vinyl magnesium bromide with thallic bromide in tetrahydrofuran in the same manner (70).

t-Butyl magnesium chloride did not give $(t\text{-Butyl})_2$ thallium chloride on reaction with thallic chloride in other at 0°C. Thallous chloride was formed.

Benzyl magnesium chloride gave di-benzyl when reacted with thallic chloride in ether; thallous chloride was also formed.

Allyl magnesium bromide, on reaction with thallic bromide in T.H.F. at 0°C, gave thallous bromide.

$(\alpha\text{-thiophenyl})_2$thallium chloride. { See Krause and Renwanz (71); } in this work this compound was prepared by the reaction of α-thiophenyl boronic acid with thallic chloride in water. The reaction takes $\sim\frac{1}{2}$ hour on shaking at room temperature, longer reaction periods result in the decomposition of the product.

Cis- and trans-$(\text{propenyl})_2$ thallium bromide (72) and $(CH_3.CH{=}C.CH_3)_2TlBr$ were prepared by the reaction of the organo-lithium compound (prepared at $\sim$ -20°C under nitrogen (73)) with $TlBr_3$, at -15°C, in ether.

Di-allyl mercury (74) on reaction with thallic chloride in ether at 0°C , did not give di-allyl thallium chloride; a mixture of $HgCl_2$ and Tl_2Cl_3 was precipitated.

Trans-$(CHCl{=}CH)_2Hg$ on reaction with thallic chloride in ether solution (75) gave trans-$(CHCl{=}CH)_2TlCl$.

Analysis. $(CH_3.CH{=}C.CH_3)_2TlBr$ requires: C, 24.36; H, 3.58 : found; C, 24.46 ; H, 3.64 %.

Trimethyl thallium (7) was prepared by reacting dimethyl thallium bromide with methyl lithium (a 10% excess) in ether under nitrogen at 0°C. The bulk of ether was removed by distillation at reduced pressure, and trimethyl thallium was distilled under high vacuum.

It was purified by repeated 'bulb to bulb' vacuum sublimation.

$$Me_2TlBr + MeLi = Me_3Tl + LiBr.$$

Triethyl thallium was prepared in the same way from diethyl thallium bromide and ethyl lithium (7).

These alkyls were stored under vacuum in small bulbs fitted with a high vacuum tap and a B.14. Quickfit Socket (Fig13). This facilitated the transfer of the alkyl on the vacuum system.

Preparation of tri-(methyl,vinyl)thallium. A solution of methyl lithium (0.04g.mol) in 25 ml of anhydrous diethyl ether was slowly added, under nitrogen, to a stirred suspension of 5g (0.018 g.mol) of divinyl thallium chloride in 25 ml of ether at ca. -5°C. After stirring for an hour, the bulk of the ether was pumped off, and the residue was fractionally sublimed on a vacuum line, using asshort a distillation path as possible to reduce decomposition. A colourless, needle-like crystalline solid was obtained, and characterised by its proton magnetic resonance spectrum in solution. From the relative peak areas in the spectrum, the molar ratio of methyl groups to vinyl groups, in the sample on which measurements were made, was found to be 1.75 : 1. It is stable in the absence of air or light, but its solutions at room temperature slowly deposit crystals of thallium.

Attempted Preparations of Trivinyl thallium.

A. An ethereal solution of vinyl lithium, prepared from phenyl lithium and tetravinyl tin (76),

$$4PhLi + Vi_4Sn \overset{ether}{=} 4ViLi + Ph_4Sn\downarrow$$

did not react with divinyl thallium chloride. Moreover, no reaction took place in boiling tetrahydrofuran.

B. In a mixture of exchanging metal alkyls it should be possible to separate the more volatile components by fractional vacuum distillation. Thus divinyl thallium chloride was reacted with phenyl lithium in ether at 0°C. The yellow suspension blackened and thallium metal was deposited. Distillation subsequently gave only a colourless volatile liquid. This was characterised by its proton resonance spectrum and the dibromide (m.p. 73°C), as styrene.

C. On reaction with n-octyl lithium, divinyl thallium chloride gave 1-decene which was characterised as the 2,4 dinitrobenzene sulphenyl chloride derivative (mixed m.p. 79.5° - 81.0°C) (77). A black precipitate of thallium metal was again formed. However, no reaction was observed between 9,lithium anthracene and divinyl thallium chloride in ether (78).

D. In the same way, an ethereal solution containing triphenyl thallium and vinyl lithium (76), on removal of the ether and vacuum distillation gave a residue of thallium, and styrene was again found to be the only volatile product.

The unusual vinylation reaction observed in these attempts might be useful in preparing various organo-vinyl derivatives.

Triphenyl thallium (7) was prepared from diphenyl thallium bromide and phenyl lithium in ether at room temperature under nitrogen. The ether was removed on a water bath at ~60°C and the residue was extracted with hot degassed benzene and filtered under nitrogen. Triphenyl thallium was precipitated from the benzene solution by adding degassed 60/80 petroleum ether. It was recrystallised in the same manner from benzene and petrol under nitrogen (m.p.166 - 7°C,with

some decomposition). (Found C,49.98; H, 4.02: $C_{18}H_{15}Tl$ requires C,49.7; H,3.46.%).

Triphenyl thallium / Trimethylamine adduct.

Triphenyl thallium (1 gm) was dissolved in dry trimethylamine (ca 5 ml), and the excess of trimethylamine was evaporated at room temperature in a stream of oxygen-free nitrogen giving a white crystalline product. (Found: C,51.07; H,5.47; N,2.96: $C_{21}H_{24}NTl$ requires: C,51.0; H,4.89; N,2.83 %). The formulation as a 1:1 complex was confirmed from the relative peak areas in the proton resonance spectrum of a carbon disulphide solution. The crystals had a negligible vapour pressure of trimethylamine at room temperature indicating that the complex is a reasonably stable one. In air it is slowly oxidised to diphenyl thallium oxide.

Monovinyl thallium dibromide(70). Divinyl thallium bromide (2g.) was boiled for 1 minute with an aqueous solution of thallic bromide (4 gms). The solution was made faintly acid with HBr to prevent hydrolysis of the thallic bromide. On cooling a light yellow precipitate separated; this was recrystallised from hot water. The proton resonance spectrum of this compound showed that it was in fact a mixture of Vi_2TlBr and $ViTlBr_2$, $ViTlBr_2$ was never obtained pure. Monovinyl thallium di-perchlorate and sulphate decompose rapidly at room temperature.

Monophenyl thallium dichloride (8) An excess of thallic chloride (4.5G 3 mols) was boiled in 6 - 8 ml of water with phenylboronic acid (0.6g. 1 mol) for 1 minute. The precipitate was filtered, then recrystallised from warm water.

All the other monoaryl thallium dichlorides were prepared in the same manner from the aryl boronic acid and thallic chloride. Aryl boronic acids were prepared by the reaction of tri-(n-butyl) borate at-80°C with the corresponding aryl Grignard reagent (79).

Analysis.

α-Napthyl thallium dichloride: found C, 30.07 ; H, 1.93 ; Cl, 17.68 $C_{10}H_7TlCl_2$ requires C, 29.85 ; H, 1.75 ; Cl, 17.62 %.

9.Phenanthryl thallium dichloride: found C, 37.01 ; H, 2.13 ; Cl, 14.55 : $C_{14}H_9TlCl_2$ requires, C,37.16 ; H, 2.05 ; Cl, 15.67 % .

4-methyl, α -napthyl thallium dichloride; found C, 31.89 ; H, 2.36 ; Cl, 17.59 : $C_{11}H_9TlCl_2$ requires C, 31.71 ; H, 2.18 ; Cl, 17.02 % .

Biphenyl thallium dichloride: found C, 33.59 ; H, 2.33 ; Cl, 16.51 ; $C_{12}H_9TlCl_2$ requires C, 33.63 ; H, 2.12 ; Cl, 16.55 %.

The mono-methyl thallium cation.

Mixtures of $Me_2Tl(ClO_4)$ with $TlCl_3$, dissolved in water, and in dimethyl sulphoxide solutions, did not show any resonances other than those from the dimethyl thallium cation and the solvent. If the $MeTl^{2+}$ cation was present it would be expected to give a spin-spin doublet with a $Tl,H(CH_3)$ coupling constant of $\sim$ 900 c/sec. .

Analysis for thallium in the solutions of trimethyl thallium.

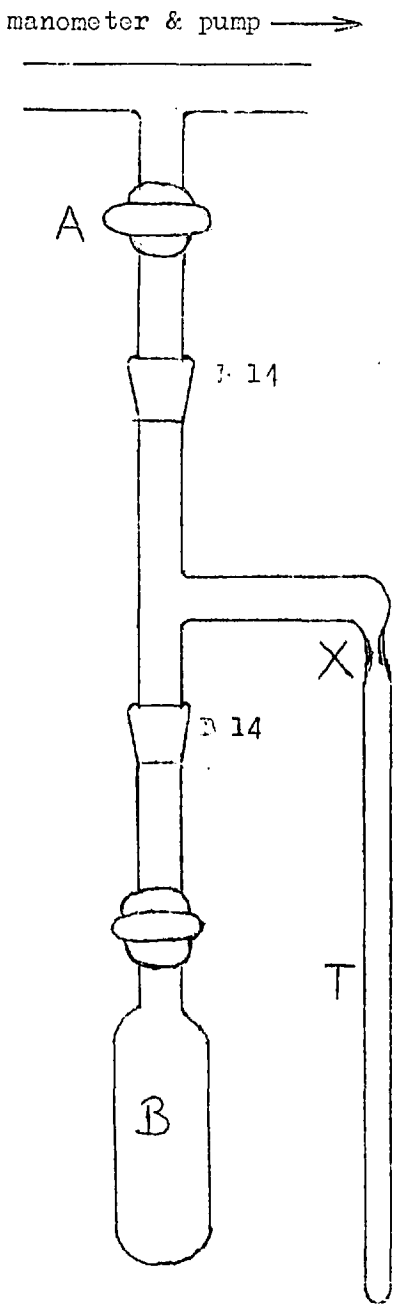
The length of solution in the nuclear magnetic resonance tube was measured and it was weighed and opened carefully under dilute nitric acid. The tube was washed out thoroughly and then reweighed. The volume of solution in the tube was calculated by weighing a known length of water in it.

The solution of dimethyl thallium nitrate was then evaporated on a steam bath and destroyed by heating with (1 : 1) nitric/sulphuric acid until all the nitric acid had been removed. The product was diluted with distilled water, then reduced with sodium sulphite and finally boiled to remove excess of sulphur dioxide, and reduced in volume to $\sim$ 10ml. The thallous solution was transferred, with washings, to a 100 ml graduated flask and made up to $\sim$ 60 ml with concentrated hydrochloric acid. 5 ml of carbon tetrachloride was added and the thallium titrated with 0.025 M - potassium iodate. (Andrews' conditions (80)).

The preparation and handling of the solutions for proton magnetic resonance study.

Trimethyl, triethyl and tri (methyl,vinyl) thallium were transferred, in vacuo to 5 mm od. nuclear magnetic resonance tubes which had previously been baked out at ca. 300°C. The apparatus used for this distillation is shown in Fig. 13 , as none of these alkyls are very stable (or very volatile) as short a distillation path as possible is necessary. After distilling the requisite quantity of trialkyl into the tube T , the solvent,

Fig.13



together with tetramethyl silane reference, was distilled from the main vacuum line (tap A) onto the trialkyl. The tube was then frozen in liquid nitrogen and sealed (whilst pumping) at X . In preparing these solutions care was taken to exclude traces of oxygen or water which could have caused the formation of catalytic impurities. The solvents were dried over lithium aluminium hydride or Linde Molecular Seives and thoroughly degassed.

Triphenyl thallium, although unstable to oxygen and water vapour can be handled for short periods in the 'open' whilst flushing nitrogen over the containing vessels. The sample of triphenyl thallium was sealed with solvent and T.M.S. , under vacuum in an n.m.r. tube.

The proton resonance spectra of the dialkyl thallium cations were measured in D_2O solution, using the sulphate or perchlorate salts. It was established that the coupling constants were independent of concentration. Due to the insolubility of many of these alkyls saturated solutions had to be used. The dialkyls gave the same coupling constants ($\pm$ 1%) in dimethyl sulphoxide as they did in water.

The tolyl and phenyl thallium dications were also studied as sulphates in D_2O. (Meta-tolyl thallium di-perchlorate was prepared once, it is a white solid, and 0.3 gm exploded on touching with a spatula, with sufficient violence to smash the author's glasses and vacuum line.) The other aryl thallium dichlorides were studied in dimethyl sulphoxide, for the fairly strong solutions used ($\sim$15% by weight) they gave coupling constants which are independant of concentration.

Tetramethyl silane was normally used as an internal reference for the non-aqueous solutions. For aquous solutions the methyl signal from t-butyl alcohol was used as an internal reference. The chemical shifts are accurate to ca. $\pm$ 0.01 p.p.m. . The coupling constants are usually accurate to $\pm$ 2.0 c/sec., although this depends very much on each individual sample since many of the lines are fairly broad ($\sim$10 c/sec.); where a much larger error is involved it is quoted.

Proton magnetic resonance spectra were measured on a Varian V4311 spectrometer at 56.45 Mc/sec., or at 40 Mc/sec. using a

Varian V4340 variable temperature probe. Decoupling experiments were carried out on a single side band proton spin-spin decoupler designed and built by Dr. Turner (81).

Appendix I.

The Exchange of Nuclear Spins between two sites.

Proton magnetic resonance spectra are modified by various rate processes (10). The chemical exchange of atoms or groups of atoms between two environments in molecules can cause the individual resonances of these to collapse if the exchange rate is fast enough. In the same way spin multiplets are collapsed by the exchange of atoms or groups of atoms between identical molecules. The simplest instance of this is the collapse of a spin spin doublet such as is observed in the proton resonance spectrum of trimethyl thallium.

It is assumed in the following very brief summary that the theory for the collapse of two chemically shifted resonances is also applicable to the collapse of the spin spin doublet of trimethyl thallium. It seems that this is true to a good approximation for the relatively slow rates observed here; for fast rates, where only a single narrow resonance is observed, a more comprehensive theory must be used (82, 83, 84).

The relation between the rate of chemical exchange and the line-shape is based on a semi-classical theory suggested by Gutowsky, McCall and Slichter (34), and later simplified by McConnell (85). The Bloch equations describe the variation of the components of the total macroscopic nuclear magnetic moment (M_x, M_y, M_z) per unit volume (10). The equations are described in terms of a coordinate system which is rotating with the applied radio frequency field. If u and v are the

transverse components of M along and perpendicular to the r.f field H_1 rotating with angular frequency ω . Also if H_1 is not too large, so that $M_z \approx M_o$ (i.e., no saturation),

$$\dot{u} + \frac{u}{T_2} + (\omega_o - \omega)\, v = 0 \quad . \quad . \quad . \quad (i)$$

$$\dot{v} + \frac{v}{T_2} - (\omega_o - \omega)\, u = -\gamma H_1 M_o \quad . \quad . \quad (ii)$$

where T_2 is the spin-spin (transverse) relaxation time, and $\omega_o = \gamma H_o$ is the Larmor precession frequency. A complex moment is defined as

$$G = u + iv$$

so that from (i) and (ii),

$$\dot{G} + \left[\frac{1}{T_2} - i(\omega_o - \omega)\right] G = -i\gamma H_1 M_o \quad . \quad . \quad (iii)$$

If there are two resonance frequencies A and B , then there will be two corresponding Larmor precession frequencies ω_A and ω_B, so that two independent macroscopic moments, are given by the equations,

$$\dot{G}_A + \alpha_A G_A = -i\gamma H_1 M_{oA} \quad . \quad . \quad . \quad (iv)$$

$$\dot{G}_B + \alpha_B G_B = -i\gamma H_1 M_{oB} \quad . \quad . \quad . \quad (v)$$

where $\alpha_A = \frac{1}{T_{2A}} - i(\omega_A - \omega)$; $\alpha_B = \frac{1}{T_{2B}} - i(\omega_B - \omega)$.

Equations (iv) and (v) were modified by McConnell (85) to take into account the exchange of nuclei, and hence the transfer of magnetisation from one spin site to the other. Nuclear exchange between positions with the same spin state will have no effect on these macroscopic moments. Thus, if a nucleus in an A position has a probability τ_A^{-1} of moving to a B position, τ_A is the mean lifetime for a nucleus on the A sites. Likewise τ_B. In the case in hand, the populations of the nuclei on the

two sites are equal, as are the relaxation times T_{2A} and T_{2B} for the two positions. Hence,

$$\dot{G}_A + \alpha_A G_A = -i\gamma H_1 M_{oA} + \tau_B^{-1} G_B = \tau_A^{-1} G_A . \quad \text{(vi)}$$

$$\dot{G}_B + \alpha_B G_B = -i\gamma H_1 M_{oB} + \tau_A^{-1} G_A - \tau_B^{-1} G_B . \quad \text{(vii)}$$

Equations (vi) and (vii) are solved by putting $\dot{G}_A = \dot{G}_B = 0$ and $M_{oA} = M_{oB} = \frac{1}{2} M_o$, the total complex moment

$$G = G_A + G_B = -i\gamma H_1 M_o \cdot \frac{\tau_A + \tau_B + \frac{1}{2}\tau_A \tau_B (\alpha_A + \alpha_B)}{(1 + \alpha_A \tau_A)(1 + \alpha_B \tau_B) - 1} \quad \text{(viii)}$$

The intensity of absorption at a frequency ω is proportional to the imaginary part of G. The transition from a spectrum of two lines to a spectrum of one line occurs when the lifetimes τ_A and τ_B are of the order $(\omega_A - \omega_B)^{-1}$. Equation (viii) was studied by Gutowsky and Holm (86) for such exchange rates. Then if the average lifetime of a group on either site is τ,

$$\tau = \frac{\tau_A \tau_B}{\tau_A + \tau_B}$$

Also if the spin-spin relaxation time is very long so that $T_2^{-1} = 0$, the line width in the absence of exchange is small compared to the separation of the two signals. { In trimethyl thallium at -60° the separation of the spin-spin doublet is $250._4$ c/sec. compared to the line width of 4 c/sec.}. Gutowsky and Holm find that the intensity of absorption is proportional to

$$\frac{(\omega_A - \omega_B)^2 \tau}{\left[\frac{1}{2}(\omega_A - \omega_B) - \omega\right]^2 + \tau^2(\omega_A - \omega)^2(\omega_B - \omega)^2} \quad \text{(ix)}$$

In terms of frequencies ($\nu = \omega/2\pi$), the shape function,

$$g(\nu) = K. \frac{\tau (\nu_A - \nu_B)^2}{\left[\frac{1}{2}(\nu_A - \nu_B) - \nu\right]^2 + 4\pi^2\tau^2(\nu_A - \nu)^2(\nu_B - \nu)^2} \quad (x)$$

where K is a normalising constant. A line shape calculated using equation (x) is shown in combination with the experimental shape in Fig.15.

For large τ , Eq. (x) gives two lines at ν_A and ν_B , and for small τ it gives one line half-way in between these. Fig.14 shows how the spectrum changes between these extremes. In the study of the trimethyl thallium exchange activation energy, the region of partial collapse where the spectrum still shows two lines was considered, and τ calculated from,

$$\frac{\text{Separation of peaks}}{\text{Separation of peaks for large } \tau} = \left[1 - \frac{1}{2\pi^2\tau^2(\nu_A - \nu_B)^2}\right]^{\frac{1}{2}} \quad (xi)$$

which is obtained from eq.(x) (10).

τ is the mean lifetime of a methyl group in a given spin state. However, the methyl groups are undergoing a chemical exchange between thalliums in the two different spin states α and β, so that they have a probability of $\frac{1}{2}$ of preserving their spin state. The mean lifetime of a methyl group between exchanges is thus $\tau/2$. In relating τ to the second order rate constant k_2 a further statistical factor of $\frac{1}{3}$ enters, since any one of the three equivalent methyl groups can undergo exchange.

$$\text{Thus } k_2 \sim \frac{3.2}{\tau} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (xii)$$

This is related to the second order rate equation,

$$\frac{d(Me_3Tl)}{dt} = -k_2(Me_3Tl)^2$$

by,

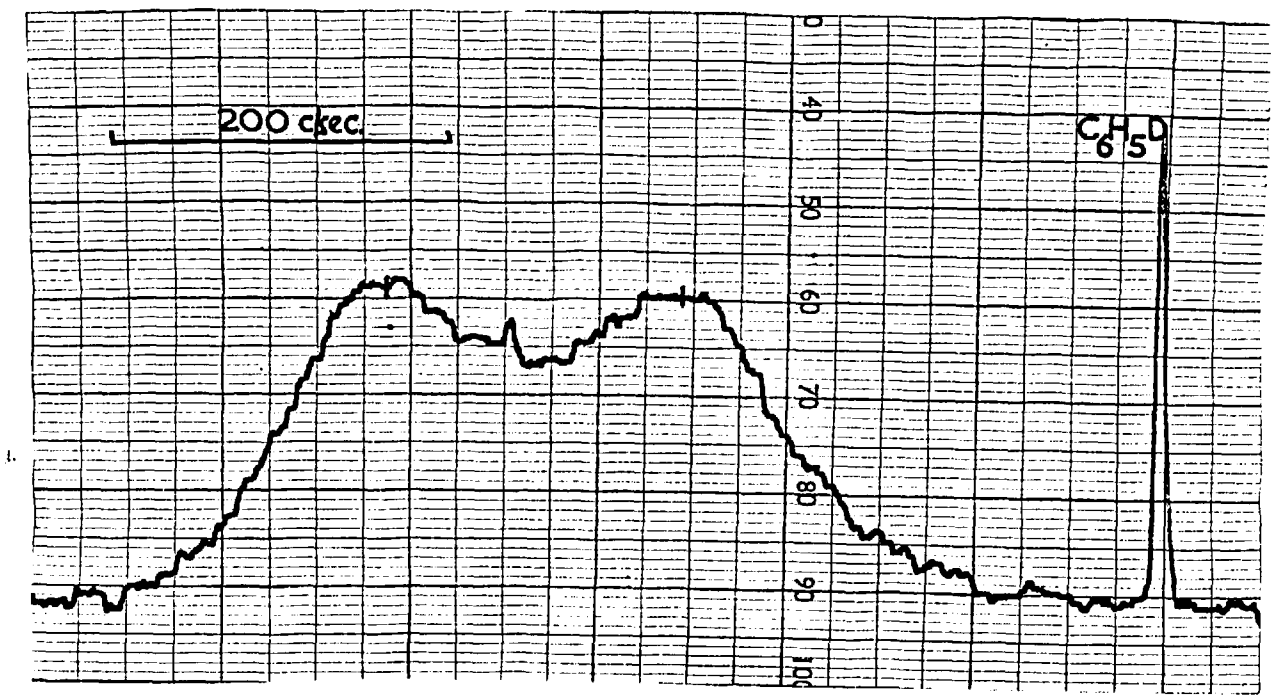
$$\frac{6}{\tau} = \frac{1}{(Me_3Tl)} \cdot \frac{d(Me_3Tl)}{dt} \quad . \quad . \quad . \quad (xiii)$$

Thus

$$k_2 = -\frac{6}{\tau(Me_3Tl)} \quad . \quad . \quad . \quad (xiv)$$

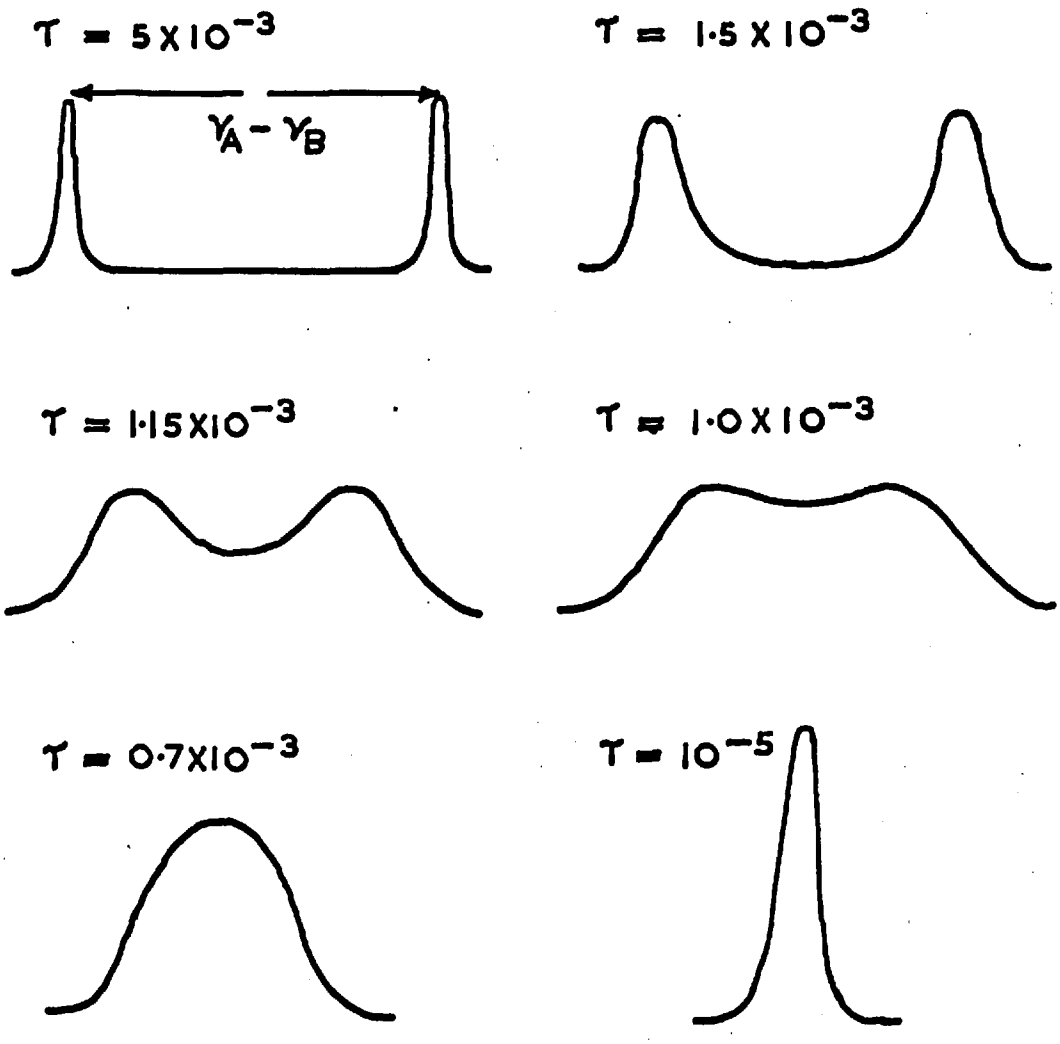
(See Loewenstein and Connor (87)).

Fig15 TYPICAL LINE SHAPE FOR A SOLUTION OF Me_3Tl IN BENZENE-d_6.



EXPERIMENTAL LINE SHAPE
CALCULATED " "

FIG 14 Line shapes for different exchange rates.



Intensities not on comparable scales.

$\nu_A - \nu_B$ = 250 c/sec. : 100 c/sec. ≃ 2 cm

APPENDIX 11.

The Determination of Relative Signs of Spin Coupling Constants.

When a molecule has more than one spin-spin coupling constant, we have the possibility that the signs of these couplings may be different. Although it is not possible at present to determine the absolute sign of any of these coupling constants experimentally*, it is possible to determine their relative signs, and from these some inferences can be made about the absolute signs (88) . The coupling between two nuclei is said to have a positive sign if it makes an anti-parallel nuclear spin configuration more stable than a parallel one.

Until 1961 the only method available for determining signs was from the mathematical analysis of complex spectra in which the chemical shifts and coupling constants were of the same magnitude. It was not possible to apply this method to first order spectra since it relies on small differences in the intensities and line positions which are unobservable here.

Recently two new methods have been developed for determining the signs in first order and near first order spectra;

(a) from double quantum spectra. In a weakly coupled spectrum, if the radio frequency power at which the spectrum is observed is greatly increased, then the normal resonances become saturated, and other lines due to double quantum transitions appear; from these, in certain circumstances, the relative signs of the couplings can be determined (89) .

* See note on Page 85.

(b) by using the method of double irradiation or spin decoupling. The technique of double irradiation was developed and first applied by Bloch and others (91) ; the application of the method to two proton nuclei was first observed by Anderson (92) , and it has since been developed to a very high degree of refinement (cf Freeman (93) et seq; Turner (81)). In a molecule if two groups of nuclei are coupled together with a coupling of J c/s, and have different chemical shifts, then by applying a strong radio frequency field ($H_1 > \frac{2\pi J}{\gamma}$) to one of these groups whilst observing the other with a weak radio frequency field, it is possible to remove the spin coupling between them. Double irradiation causes the nuclei of a group in a particular set of spin states to undergo very frequent transitions between the spin states; this effectively decouples the nuclei from the rest of the system, as the coupled nuclei can no longer follow these rapid transitions.

The first application of spin decoupling to the determination of the relative signs of coupling constants was carried out on the Et_2Tl^+ cation (90) ; this is a particularly simple example well suited to explain the method. The signs of $J_{Tl,H(CH_2)}$ and $J_{Tl,H(CH_3)}$ in the Et_2Tl^+ cation can either be the same or opposite.

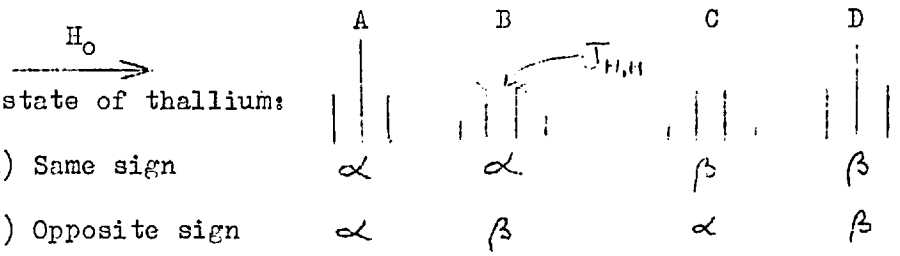
Multiplet spectra arise from the nuclei 'seeing' the nuclei to which they are coupled in different orientations in the external magnetic field H_o . Thus in an ethyl group the CH_3 sees the CH_2 in the following spin states

		$\beta\alpha$	
$\xrightarrow{H_o}$	$\alpha\alpha$	$\alpha\beta$	$\beta\beta$
Intensity	1	2	1

and the CH_2 sees the CH_3 as

H_0 ⟶	$\alpha\alpha\alpha$	$\beta\alpha\alpha$ $\alpha\beta\alpha$ $\alpha\alpha\beta$	$\beta\beta\alpha$ $\beta\alpha\beta$ $\alpha\beta\beta$	$\beta\beta\beta$
Intensity	1	3	3	1

In addition to these, each group sees the thallium nuclei in either an α or a β orientation, so that the triplet CH_3 and quartet CH_2 are split into further doublets. The spectrum is shown in Figs.10B,16, it can be represented diagramatically as



If $J_{Tl,H(CH_3)}$ is arbitarily taken to have a positive sign then the resonance A to lower field in the spectrum, corresponding to the higher energy, has the thallium in the α spin state . If $J_{Tl,H(CH_2)}$ also has a positive sign, then similarly, the lower field signal will again be assigned to thallium in an α spin state (a). However, if $J_{Tl,H(CH_2)}$ has a negative sign then the thallium in the β spin state will lie to lower field (b). Proton double irradiation of this system only removes the H,H couplings, and moreover only those couplings where the protons see the thallium in the same spin state. The Tl,H couplings will, for all normal radio frequency powers, remain unaffected. Thus if we irradiate group A, then if the signs of the Tl,H couplings are the same, group B will collapse to a single line; however, if these have opposite signs then group C will collapse to a

single line. The latter is found to be the case, so that $J_{Tl,H(CH_2)}$ and $J_{Tl,H(CH_3)}$ have opposite signs.

In the $PhTl^{2+}$ cation the ortho-meta-, and para- Tl,H couplings have been found by decoupling to have the same signs. If the low field doublet A (Fig16) from the ortho-proton is irradiated whilst observing the triplet B from the meta-proton, then the triplet B collapses to a doublet since it still remains coupled to the para-proton. Likewise irradiation of B whilst observing the para-proton C collapses this to a single line (the H,H meta coupling is not visible).

In H,H couplings there is both experimental (94) and theoretical evidence (41) for supposing that the vicinal couplings have a positive sign. [Following a suggestion by Karplus (88), Anet (94) has demonstrated by spin decoupling that $J_{C13,H}$ and $J_{H,D(gem)}$ have opposite signs, and since $J_{C13,H}$ has been shown theoretically to be largely due to the Fermi Contact term which has a positive sign, it follows that $J_{H,H(gem)}$ is negative. Further experiments have demonstrated that the vicinal and geminal H,H couplings have opposite signs (95) so the vicinal coupling is probably positive .] In view of this evidence $J_{H,H(vicinal)}$ is taken to have a positive sign and $J_{H,H(geminal)}$ a negative sign. The same convention will be adopted with the Tl,H coupling constants; it would be possible to check this assignment by double irradiation of the Tl^{205} resonance spectrum, whilst observing the H^1 resonance spectrum.

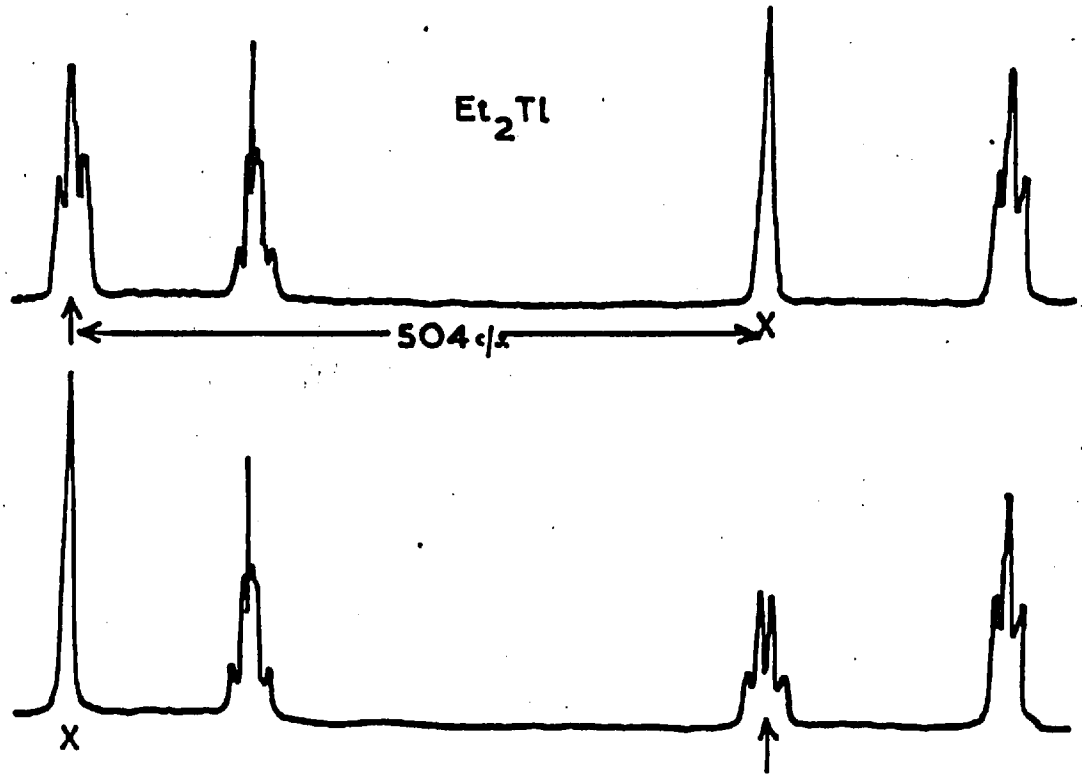
NOTE.

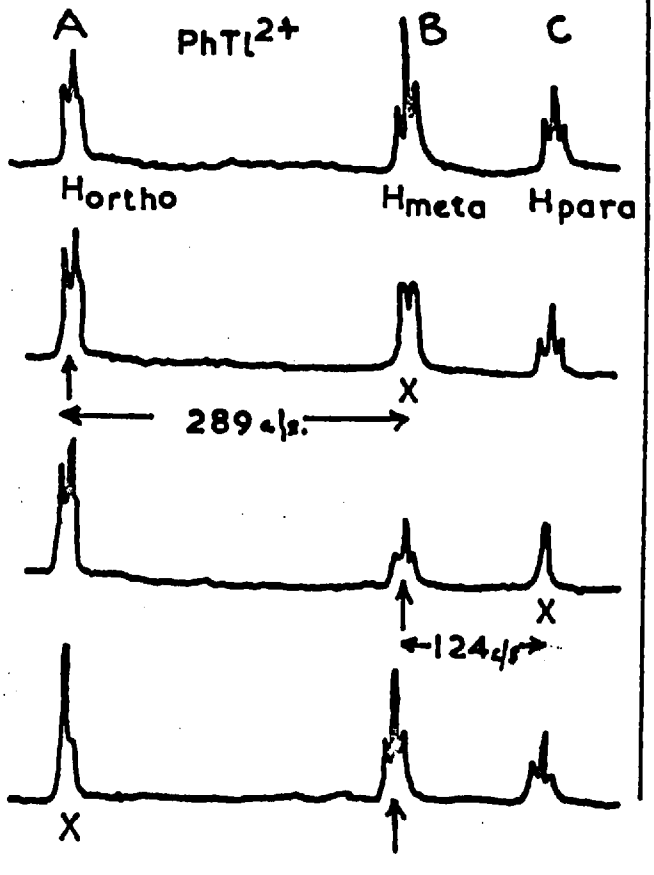
The absolute sign of the coupling constant J.

Very recently it has been possible to show that the ortho H,H coupling constant in para-nitrotoluene is absolutely positive (96). This was achieved by applying a strong electric field (24 kv/cm.) across the n.m.r. sample and observing the effect of this field on J.

This absolute positive sign for the H,H(ortho) coupling constant is in agreement with the assumed positive H,H vicinal coupling constant adopted here.

FIG 16 SPIN DECOUPLING EXAMPLES.





↑ IRRADIATED GROUP.

X OBSERVED GROUP.

FIELD INCREASES LEFT TO RIGHT.

ONLY LOW FIELD HALF OF $PhTl^{2+}$ SPECTRUM SHOWN

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987. *Proton Magnetic Resonance Spectra of Grignard Reagents and Related Metal Alkyls.*

By D. F. Evans and J. P. Maher.

The proton resonance spectra of ethereal solutions of methyl, ethyl, and propyl Grignard reagents closely resemble those of the corresponding dialkyls. The small differences found have been studied in detail for "methylmagnesium iodide" and dimethylmagnesium. These results support other evidence that Grignard reagents are better represented as R_2Mg,MgX_2 than as RMgX. Proton resonance data are also presented for related mercury, zinc, and cadmium compounds.

Grignard reagents are usually formulated as RMgX. However, since their discovery by Grignard in 1900, there has been considerable speculation about the species present in solution; a comprehensive review of work up to 1950 has been given by Kharasch and Reinmuth.[1] The addition of dioxan to ethereal Grignard solutions precipitates the magnesium halide and "RMgX" and leaves the dialkylmagnesium in solution, suggesting the presence of an equilibrium mixture: $2RMgX \rightleftharpoons R_2Mg + MgX_2$. However, this Schlenk equilibrium [2] seems very much over-simplified.

More recently Dessy and his collaborators [3] measured the dielectric constants and conductivities of Grignard solutions and of the (apparently identical) solutions prepared by mixing compounds R_2Mg with MgX_2. They concluded that Grignard reagents were better represented as R_2Mg,MgX_2. In agreement with this, no exchange was observed between $^*MgBr_2$ (radioactive magnesium) and diethylmagnesium in ethereal solution,[4] which seems to preclude the Schlenk equilibrium.

The elegant work of Roberts and his collaborators [5] on the proton magnetic resonance spectra of allyl and related Grignard reagents was mainly concerned with the structure of the organic group. However, they noted that "dibutenylmagnesium shows the same chemical shifts as does the ordinary Grignard. This can be taken as an argument against the Grignard formula RMgBr since the bromine ought to have some influence on the chemical shift of the CH_2 resonance."

In the present work the proton magnetic resonance spectra of Grignard reagents and related compounds has been studied in further detail.

Experimental

Solutions of Grignard reagents and dialkylmagnesiums were prepared *in vacuo* in the apparatus shown in Fig. 1. In the preparation of the Grignard solutions, the alkyl halide and an excess of ether were distilled on to the magnesium turnings (baked *in vacuo* at ~300°), and the apparatus was sealed off at point C. A rapid reaction occurred on shaking at 0°. The apparatus was again evacuated, through limb A1, the break-seal (B) being broken, and the ether and any excess of alkyl halide were thus removed. A quantity of ether containing a small amount of tetramethylsilane was distilled into the apparatus, which was then sealed at point C1. A small portion of the mixture was filtered through the sinter S, and sealed off (at C2) in the nuclear magnetic resonance tube T. In preliminary experiments, where the Grignard solutions were prepared and transferred under oxygen-free nitrogen, irreproducible nuclear magnetic resonance spectra were obtained.

The dialkylmagnesiums were prepared similarly, from magnesium turnings and an ethereal solution of the appropriate dialkylmercury, which were shaken together at room temperature for about 3 days. For very dilute solutions, a trace of mercury was added to initiate the reaction.

The remaining compounds were prepared and purified by standard procedures. Measurements were made at 56·45 Mc./sec. on a Varian V4311 spectrometer, tetramethylsilane being normally used as an internal reference. The τ values are accurate to *ca.* $\pm$0·01 p.p.m.

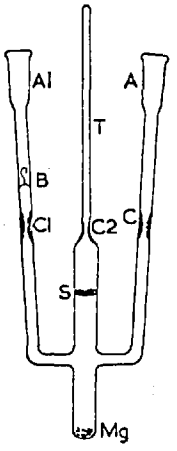


FIG. 1. Apparatus used in preparation of Grignard and dialkylmagnesium solutions.

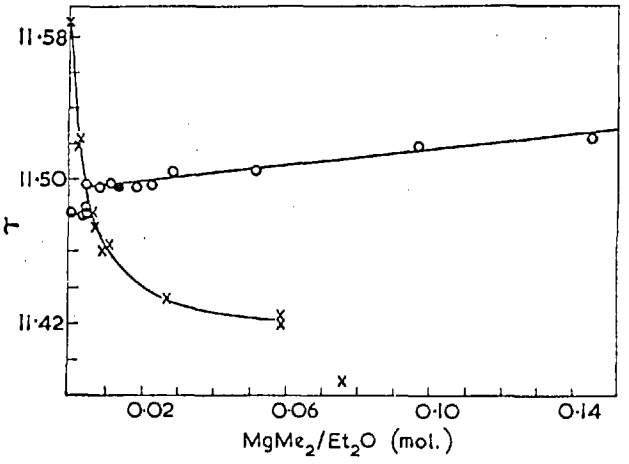


FIG. 2. Concentration-dependence for the chemical shift (τ) of diethyl ether solutions of $MgMe_2$ and " MeMgI."

○ Methyl Grignard solution. × $MgMe_2$. ● Grignard solution containing 4 mol. excess of MgI_2.

RESULTS AND DISCUSSION

With mercury, all three species R_2Hg, RHgX, and RHg^+ can be observed, and the results obtained for these species are presented in Table 1. As expected, there are very large changes in the proton resonance spectrum in going from R_2Hg to RHgX or HgR^+. These changes can be partly attributed to the inductive effect of the electronegative halogen atom or the (formal) positive change of the cation. However, for the ethylmercuric halides the δ values increase slightly in going from the chloride to the iodide, which is the opposite order to that expected from electronegativity considerations. This

TABLE 1.

Compound	τCH_3	Compound	τCH_2	τCH_3	$\tau CH_3 - \tau CH_2$ (δ)
$HgMe_2$ (pure)	9·714	Et_2Hg (CH_2Cl_2)	8·996	8·706	−0·291
MeHgCl (CH_2Cl_2)	8·908	EtHgCl (CH_2Cl_2)	8·026	8·652	+0·626
$MeHgClO_4$ (D_2O)	8·79 *	EtHgBr (CH_2Cl_2)	7·979	8·635	+0·656
		EtHgI (CH_2Cl_2)	7·897	8·571	+0·674
		$EtHgClO_4$ (D_2O)	7·71 *	8·69 *	+0·878

* Based on $\tau CMe_3 \cdot OH$ in water = 8·69,[6] $J(^{199}Hg–H)$ are: $HgMe_2$ 102·5, MeHgCl 202·4, and $MeHgClO_4$ 260·2 c./sec.

effect could be explained on the basis of π-bonding between the mercury atom and the halogen atom, but in addition there may well be long-range deshielding caused by the magnetically anisotropic Hg–X bonds, which will be largest for ethylmercuric iodide (cf. McConnell,[7] Schneider [8]).

In contrast to these results the proton resonance spectra of methyl, ethyl, and n-propyl Grignard reagents closely resemble those of the corresponding dialkylmagnesiums (see Tables 2 and 3), indicating the absence of appreciable quantities of the species RMgX, but consistent with the formulation R_2Mg,MgX_2. Small concentration-dependent differences are observed, however, which were studied for dimethylmagnesium and " MeMgI," and the results are plotted in Fig. 2. The τ values for dimethylmagnesium in ether show an appreciable concentration-dependence, especially at high dilutions, which can be attributed plausibly to the dissociation of polymeric species on dilution. The concentration-dependence for the Grignard reagent, on the other hand, is very small over a considerable

concentration range. At high dilution an apparent drop in the values was observed, but this may be due to impurities since the reproducibility of the results was less than at higher concentrations. (No comparable effect was observed with dimethylmagnesium which is easier to obtain pure.) This very small concentration-dependence, together with the fact that the curves for dimethylmagnesium and " MeMgI " curves, when extrapolated, do not afford the same τ value at infinite dilution, suggests that the complex Me_2Mg,MgI_2 is stable. In agreement, a solution containing a large excess of magnesium iodide gave a value which, within experimental error, fell on the Grignard curve (Fig. 2), indicating that the equilibrium $Me_2Mg + MgI_2 \rightleftharpoons Me_2Mg,MgI_2$ lies well to the right.

TABLE 2.

$MgEt_2/Et_2O$ (mol.)	τCH_3	τCH_2	$MgEt_2/Et_2O$ (mol.)	τCH_3	τCH_2
	For $MgEt_2$			For " EtMgBr "	
0·376	8·793	10·620	0·148	8·849	10·674
0·103	8·801	10·640	0·085	8·836	10·665
0·016	8·747	10·674	0·020	8·806	10·626
Satd.*	8·840	10·84			

* In dioxan.

TABLE 3.

$MgPr^n_2/Et_2O$ (mol.)	τCH_2	τCH_2	τCH_3		$MgPr^n_2/Et_2O$ (mol.)	τCH_2	τCH_2	τCH_3
	For $MgPr^n_2$							
0·111	10·566	8·500	9·087	" Pr^nMgCl "	0·172	10·464	8·362	9·080
<0·04	10·595	8·495	9·100	" Pr^nMgBr "	0·081	10·507	8·498	9·067
Satd.*	10·665	8·536	9·113	" Pr^nMgI "	0·041	10·483	—	9·053

* In dioxan.

TABLE 4.

Solvent	EtZnI		$ZnEt_2$		$CdEt_2$	
	τCH_2	τCH_3	τCH_2	τCH_3	τCH_2	τCH_3
None	—	—	9·608	8·854	9·471	8·716
Et_2O	9·651	~8·78	9·778	8·874	9·317	8·736
Dioxan	9·740	8·897	—	—	9·688	8·760
CH_2Cl_2	—	—	9·744	8·87	9·528	8·728
C_6H_6	—	—	9·851	9·064	—	—

Although the present results are in agreement with previous evidence that Grignard reagents (in solution) should be formulated as R_2Mg,MgX_2 rather than RMgX, it may be noted that they do not provide information about numerous finer details of Grignard solutions, such as the extent of solvation by the ether, the bonding between R_2Mg and MgX_2, the degree of polymerisation of the species, and the nature of the ions present.

The proton resonance spectrum of ethylzinc iodide in ether is very similar to that of diethylzinc in ether, indicating that, in solution, this reagent should similarly be formulated as Et_2Zn,ZnI_2. The results obtained, together with those for dilute solutions of diethylzinc and -cadmium in various solvents are presented in Table 4.

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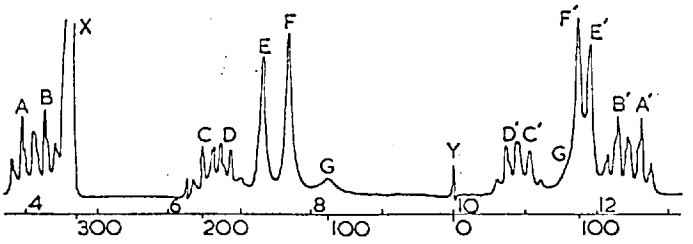
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coupling constants and chemical shifts for all four trialkyls are given in the Table, and a typical spectrum is shown in the Figure.

The ^{205}Tl-(H)CH_3 coupling constants are uniformly greater than the ^{205}Tl-(H)CH_2 coupling constants. This has previously been observed for ethyl groups attached to heavy metals such as lead[2] and mercury[3] which have nuclei with spin ½. It is also probable that the two coupling constants, ^{205}Tl-(H)CH_3 and ^{205}Tl-(H)CH_2, have opposite signs, as in the diethylthallium cation. In this cation, as in triethylthallium itself at low temperatures, the thallium nuclei split the proton resonances into doublets. Together with the smaller splitting within each ethyl group, this gives rise to two outer CH_3 triplets and two inner CH_2 quadruplets. By using the proton-spin decoupling apparatus constructed by Turner,[4] it was found that an inner CH_2 quadruplet appeared as a single line when the *distant* CH_3 triplet was simultaneously subjected to an intense radio-frequency field, and *vice versa*. This shows unambiguously that the two Tl–H coupling constants have opposite signs. This technique should be useful in obtaining relative signs of coupling constants in spectra where the separations between the groups are large compared to the splittings within them.

Chemical evidence for mixed alkyl formation was also obtained, since hydrolysis of a mixture of trimethyl- and triethyl-thallium gave a solution containing the stable unsymmetrical cation $TlMeEt^+$, in addition to the $TlMe_2^+$ and $TlEt_2^+$ cations. This mixed species was also detected by its proton-resonance spectrum (at room temperature).



Top scale = τ (p.p.m.). Lower scale = cycles/sec.

Proton magnetic resonance spectrum of a mixture of trimethyl- and triethyl-thallium in dichloromethane at −85°. Et *groups:* A,A′, CH_3 in $TlMe_2Et$; B,B′, CH_3 in $TlMeEt_2$; C,C′, CH_2 in $TlMe_2Et$; D,D′, CH_2 in $TlMeEt_2$. Me *groups*, E,E′, $TlMe_3$; F,F′, $TlMe_2Et$; G,G′, $TlMeEt_2$. *There is considerable overlap of the lines arising from the* Et *groups. Differential splitting by the two thallium isotopes is visible for* A,A′ *and* B,B′.

X = CH_2Cl_2. Y = $SiMe_4$.

Measurements were made at 56·4 Mc. on a Varian V4300B spectrometer, with a Varian V-4340 variable temperature probe.

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Biosynthesis of Aromatic Substances from Acetyl- and Malonyl-coenzyme A

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THE appearance of the Communication by Bentley and Keil[1] on the function of malonate as a part-precursor of penicillic acid (I) prompts us to report our work on the biosynthesis of 6-methylsalicylic acid (III). Penicillic acid is one of a number of substances demonstrably[2] or hypothetically derived from "acetate"—presumed to be in the form of acetyl-coenzyme A—by way of orsellinic acid (II) in

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Proton Magnetic Resonance Spectra of Thallium Trialkyls; Chemical Exchange and Formation of Mixed Alkyls

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Thallium has two isotopes, both with nuclear spin $\frac{1}{2}$, and with very similar nuclear magnetic moments: ^{203}Tl (29·5% abundant, $\mu = 1{\cdot}5960$) and ^{205}Tl (70·5% abundant, $\mu = 1{\cdot}6114$). These isotopes produce large spin–spin splittings in the proton resonance spectra of dialkyl- and diaryl-thallium cations in aqueous solution. The results obtained will be submitted for publication elsewhere. However, trimethyl- and triethyl-thallium in solvents such as dichloromethane and toluene give only a single broad proton-resonance line at room temperature. At −60° to −100° the spectra resemble those for the dimethyl- and diethyl-thallium cations, indicating that a rapid chemical exchange is occurring at room temperature. For trimethylthallium in dichloromethane, the collapse of the spin multiplets due to splitting by the thallium nuclei with increase in temperature enables[1] the activation energy for the exchange to be estimated as 6 ± 1 kcal. mole^{-1}. This exchange, which was found to be concentration- and solvent-dependent, presumably involves interchange of methyl (or ethyl) groups between two monomeric trialkylthallium molecules.

In agreement with this interpretation, mixtures of trimethyl- and triethyl-thallium in dichloromethane, when cooled to −85°, give proton-resonance lines additional to those due to the pure trialkyls. By varying the initial concentrations of the two components, it was possible to detect the presence of the mixed alkyls $TlMe_2Et$ and $TlMeEt_2$. The spin–spin

Proton magnetic resonance results for trialkyl thalliums in dichloromethane at ca. −85°.

Compound	Me group ^{205}Tl–H coupling constant (cycle/sec.*)	Me group τ (p.p.m.)	Et group ^{205}Tl–H(CH_2) coupling constant (cycle/sec.*)	Et group τ CH_2 (p.p.m.)	Et group ^{205}Tl–H(CH_3) coupling constant (cycle/sec.)	Et group τ CH_3 (p.p.m.)
$TlMe_3$	250·$_8$	9·48	—	—	—	—
$TlMe_2Et$	223·$_0$	9·58	242·$_4$	8·66	472·$_7$	8·20
$TlMeEt_2$	186·$_9$	9·73	218·$_8$	8·71	441·$_5$	8·18
$TlEt_3$	—	—	198·$_2$	8·71	396·$_1$	8·21

The H(CH_2)–H(CH_3) coupling constant was 7·7 ± 0·3 cycle/sec. in all the ethyl derivatives.
* These values will be slightly low (by < 1 cycle/sec.) since the $^{205}Tl/^{203}Tl$ splitting was not resolved.

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