103. *Thallium–Proton Spin–Spin Coupling Constants.*

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^{205}Tl–H coupling constants are reported for a wide variety of organothallium compounds. In many cases, the relative signs of the coupling constants have been determined by double irradiation. In the series, R_3Tl, R_2Tl^+, and RTl^{2+}, the coupling constants increase approximately as 1 : 1·7 : 4·0. Except for geminal coupling, the Tl–H coupling constants closely parallel the corresponding H–H coupling constants, being *ca.* 60 times larger in the R_2Tl^+ cations. It is concluded that the predominant mechanism in thallium–proton coupling is the Fermi-contact interaction.

LARGE ^{203,205}Tl–H spin–spin coupling constants have been observed in organo thallium compounds.[1-3] Because of the great simplicity of the spectra, which is due to the large and nearly equal magnetic moments of these two thallium isotopes, and to the lack of any naturally occurring isotopes without a spin of ½, these compounds provide an almost ideal series for studying some of the factors involved in heavy metal–proton coupling constants.

[1] Maher and Evans, *Proc. Chem. Soc.*, 1961, 208.
[2] Maher and Evans, *Proc. Chem. Soc.*, 1963, 176.
[3] Maher and Evans, *J.*, 1963, 5534.

It was recently suggested[3] that Tl–H coupling constants involve essentially the same mechanism as H–H coupling constants, that is *via* Fermi contact, by using the 6*s*-orbital of the thallium atom. This Paper presents ^{205}Tl–H coupling constants (given below, for simplicity, without the superscript) for a wide variety of organothallium compounds. The striking similarity between these coupling constants, and the analogous H–H coupling constants, strongly supports the above suggestion.

EXPERIMENTAL

Dialkyl- and Diaryl-thallium Bromides.—Thallic bromide solution (obtained by adding bromine to a suspension of thallous bromide in tetrahydrofuran at 0°) was treated with the appropriate Grignard reagent at 0°. After hydrolysis with ammonium bromide solution, the solid product was extracted with hot 1 : 1 aqueous ammonia or warm pyridine.

Di-(*cis*- and *trans*-propenyl)thallium bromide [4] and di-(*trans*-but-2-enyl)thallium bromide were prepared from the appropriate organolithium compound and thallic bromide in ether at *ca.* $-20°$.

Di-(trans-*but-2-enyl)thallium bromide* is new (Found: C, 24·5; H, 3·6. C_8H_4BrTl requires C, 24·4; H, 3·6%).

Vinylthallium Dibromide.[5]—Divinylthallium bromide (2 g.) was boiled for 1 min. with 40% aqueous thallic bromide (10 ml.), slightly acidified with hydrobromic acid. On cooling, a light yellow precipitate separated, which was recrystallized from water. The proton resonance spectrum of this compound showed that it was a mixture of divinylthallium bromide and vinylthallium dibromide; the latter was never obtained pure.

Monoarylthallium dichlorides were prepared by shaking an excess of aqueous thallic chloride with the corresponding arylboronic acid. [2-Thienylboronic acid, however, gave the known [6] di-(2-thienyl)thallium chloride.] Thus were obtained:

1-*Naphthylthallium dichloride* (Found: C, 30·1; H, 1·9; Cl, 17·7. $C_{10}H_7Cl_2Tl$ requires C, 29·85; H, 1·75; Cl, 17·6%).

9-*Phenanthrylthallium dichloride* (Found: C, 37·0; H, 2·1. $C_{14}H_9Cl_2Tl$ requires C, 37·2; H, 2·05%).

4-*Methyl*-1-*naphthylthallium dichloride* (Found: C, 31·9; H, 2·4; Cl, 17·6. $C_{11}H_9Cl_2Tl$ requires C, 31·7; H, 2·2; Cl, 17·0%).

4,7-*Dimethyl*-1-*naphthylthallium dichloride* (Found: C, 34·3; H, 2·6. $C_{12}H_{11}Cl_2Tl$ requires C, 33·5; H, 2·6%).

4-*Biphenylylthallium dichloride* (Found: C, 33·6; H, 2·3; Cl, 16·5. $C_{12}H_9Cl_2Tl$ requires C, 33·6; H, 2·1; Cl, 16·55%).

Sulphates and perchlorates were obtained from the bromides by metathesis with an aqueous solution of silver sulphate or perchlorate. Only the diarylthallium sulphates were studied, since 0·3 g. of *m*-tolylthallium diperchlorate exploded with extreme violence on being touched with a spatula.

Proton magnetic resonance spectra were measured on a Varian V4311 spectrometer at 56·45 Mc./sec., or at 40 Mc./sec. with a Varian V4340 variable-temperature probe. The dialkylthallium cations, and the phenylthallium dications, were studied in D_2O solution, as the perchlorate or sulphate. The coupling constants were virtually independent of concentration. The other arylthallium dichlorides were studied in dimethyl sulphoxide or [$^2H_6$]dimethyl sulphoxide solutions. For the concentrated solutions used (~10—20%), these coupling constants were also virtually independent of concentration. The majority of the spectra were "first-order," and analysis was normally straightforward. Assignments were based on intensity considerations, the observed proton–proton coupling, and, where necessary, the study of alkyl-substituted derivatives. When the coupling constants were large, differential splitting by the two thallium isotopes could often be detected. Where this splitting was not resolved, the error in assuming that the observed coupling corresponds to that produced by the more abundant ^{205}Tl isotope is very small. The relative signs of the coupling constants were obtained by double irradiation [1] in the apparatus constructed by Turner.[7] These experiments were unambiguous and straightforward, and details are therefore not given. It is now clear that

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[4] Nesmayanov, *Bull. Acad. Sci. U.S.S.R.*, 1959, 1216.

[5] Nesmayanov, Borisov, Sobeleva, and Golubeva, *Bull. Acad. Sci. U.S.S.R.*, 1958, 1490.

[6] Krause and Renwanz, *Ber.*, 1929, **62**, 1710.

[7] Turner, *J.*, 1962, 847.

vicinal H–H coupling constants normally have an absolute positive sign.[8,9] In presenting the results, we have assumed that the vicinal Tl–H coupling constants also have a positive sign. This assumption could be tested by heteronuclear (Tl, H) double irradiation.

RESULTS AND DISCUSSION

Variation of the Tl–H *Coupling Constants in the Series,* R_3Tl, R_2Tl^+, *and* RTl^{2+}.—The uniform increase in the magnitude of the coupling constants in this series is a general feature for all the organothallium compounds studied (Table 1). On the basis of the Fermi contact term, this increase can be qualitatively interpreted as due to the increase in both the *s*-character of the outer electrons of the thallium atom, and in the effective nuclear charge Z_{eff} of the thallium atom. Z_{eff} is equal to $(Z_0Z)^{\frac{1}{2}}$, where Z is the real nuclear charge, and Z_0 is the Slater screened nuclear charge. If it is assumed that the coupling constants are directly proportional to the *s*-character,[10] and also to $(Z_{eff})^{3,11}$ then the calculated ratios for R_3Tl (sp^2-hybridization), R_2Tl^+ (sp-hybridization), and RTl^{2+} (s-hybridization) are 1 : 1·8 : 4·3. The excellent agreement with the observed ratios (Table 2) need not be taken very seriously, since a number of factors have been neglected or given very approximate values in the above calculation. In particular, the coupling between non-directly bonded atoms involves a number of different exchange integrals,[12] and also it is unlikely that in the (solvated) RTl^{2+} ion the Tl–C bond has 100% *s*-character.

TABLE 1.

Variation in the Tl–H coupling constants (in c./sec.) in the series R_3Tl, R_2Tl^+, and RTl^{2+}.

R	H position	R_3Tl	R_2Tl^+	RTl^{2+}	R	H position	R_3Tl	R_2Tl^+
Phenyl	*ortho*	+259 *	+451 †	+948 †	Ethyl	CH_2	−198 ‡	−340 †
	meta	+80 ± 5	+139	+365		CH_3	+396	+628
	para	+35 ± 5	+51·$_7$	+123	Methyl	CH_3	−251 ‡	−403 ‡
Vinyl	*trans*		+1618 ± 5†	+3750 ± 10 †				
	cis		+805 ± 5	+1806 ± 10				
	gem		+842 ± 5	+2004 ± 10				

* In trimethylamine. † As the perchlorate in D_2O.. ‡ In CH_2Cl_2

TABLE 2.

Average ratios between the Tl–H coupling constants in Table 1.

R	R_3Tl	R_2Tl^+	R_2Tl^+	R	RTl_3	R_2Tl^+
Phenyl	1	1·7	4·0	Ethyl	1	1·6
Vinyl	1	(1·7)	2·3 (3·9)	Methyl	1	1·65

Very recently Hatton, Schneider, and Siebrand[13] have reported ^{199}Hg–H coupling constants in $CH_3·HgX$ and $CH_3·CH_2·HgX$ compounds. They interpreted their results in terms of changes in hybridization and in optical hyperfine structure constants, assuming a Fermi contact interaction.

The Phenylthalliums.—If the Tl–H coupling constants in the $PhTl^{2+}$ cation (Table 1) are divided by ~130 (or those in Ph_3Tl and in the Ph_2Tl^+ cation by the appropriately reduced factors), then the values obtained are similar in both magnitude and sign to the corresponding H–H coupling constants in substituted benzenes. These are $J_{H-H(ortho)}$ + 6—9; $J_{H-H(meta)}$ + 1—3; $J_{H-H(para)}$ + 0—1 c./sec. (ref. 8). A factor of ~130 is also found if the $TlH(CH_3)$ coupling constants in the *o*- and *p*-tolylthallium dications (Table 3) are compared with the corresponding $H-H(CH_3)$ couplings in mesitylene (0·89 and 0·45 c/sec., respectively).[14]

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[8] Banwell and Sheppard, *Discuss. Faraday Soc.*, 1962, **34**, 115.

[9] Anet, *J. Amer. Chem. Soc.*, 1962, **84**, 3767; Buckingham and McLauchlan, *Proc. Chem. Soc.*, 1963, 144.

[10] Juan and Gutowsky, *J. Chem. Phys.*, 1962, **37**, 2198, and references therein.

[11] Schneider and Buckingham, *Discuss. Faraday Soc.*, 1962, **34**, 147.

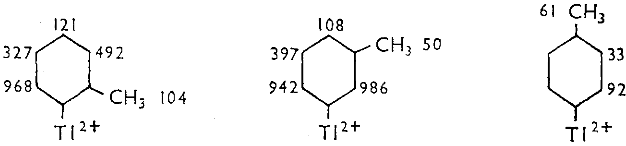
[12] Karplus, *J. Chem. Phys.*, 1959, **30**, 11.

[13] Hatton, Schneider, and Siebrand, *J. Chem. Phys.*, 1963, **39**, 1330.

[14] Acrivos, *Mol. Phys.*, 1962, **5**, 1.

TABLE 3.

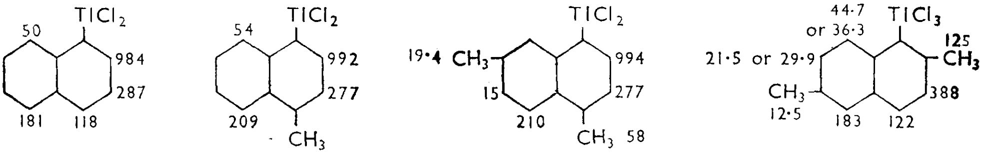
Tl–H coupling constants in the *o*-, *m*-, and *p*-tolythallium dications



H–H coupling constants in aromatic and unsaturated systems are transmitted in two ways, *via* the σ-electrons and, as a result of σ–π configuration interaction, *via* the π-electrons.[8] If only the latter mechanism is involved, replacement of a directly bonded proton by a methyl group should theoretically lead to an H–H(CH_3) coupling constant approximately equal in magnitude to the original H–H coupling constant, but of opposite sign.[8,15] The results in Tables 1 and 2 therefore suggest that, as for the corresponding H–H coupling constants, the thallium coupling to the *ortho*- and *meta*-ring protons is transmitted mainly *via* the σ-electrons of the benzene ring. In contrast, for the *para*-coupling, transmission *via* the π-electrons is important. Although coupling through one further bond is involved, the Tl–$H_{(para\text{-}CH_3)}$ coupling constant is greater than the Tl–$H_{(meta\text{-}CH_3)}$ coupling constant. This is consistent with valence-bond and molecular-orbital calculations of the π-contribution to H–H coupling constants by McConnell [16] and Acrivos.[14] (No experimental value for an H–$H_{(meta\text{-}CH_3)}$ coupling constant has been reported.) The theoretical ratios for $J_{H\text{-}H(para\text{-}CH_3)}/J_{H\text{-}H(meta\text{-}CH_3)}$ are 1·1 (McConnell) and 1·3 (Acrivos), as compared with 1·2 found experimentally for the Tl–H(CH_3) coupling constants.

TABLE 4.

Tl–H coupling constants in the 1-naphthylthallium dichlorides.



It has been pointed out by Banwell and Sheppard [8] that $J_{H\text{-}H(meta)}$ is unusually large for a σ-bond mechanism through four bonds. This is also true for $J_{Tl\text{-}H(meta)}$, since in the $Pr^n_2Tl^+$ and $Bu^i_2Tl^+$ cations the Tl–H(γ-CH_3) coupling constants are only +20·4 and +16·0 c./sec., respectively.

Di-(2-thienyl)thallium Sulphate.—In this compound, the Tl–H coupling constants are: $J_{Tl\text{-}H(3)}$ + 304; $J_{Tl\text{-}H(4)}$ + 105; $J_{Tl\text{-}H(6)}$ + 197 c./sec. In substituted thiophens, the corresponding H–H coupling constants are: J_{23} + 4·9—5·8; J_{24} + 1·2—1·7; J_{25} + 3·2—3·7 c./sec.[15] As in the diphenylthallium cation, the Tl–H coupling constants all have the same sign, and are approximately 60 times the corresponding H–H coupling constants.

1-*Naphthylthallium Dichlorides.*—The results obtained are given diagrammatically in Table 4. In the spectrum of 1-naphthylthallium dichloride, five Tl–H coupling constants can be distinguished (Fig. 1). From the spectra of various methyl-substituted derivatives, it has been possible to detect coupling from the thallium nucleus to protons in all seven positions of the naphthalene ring. The coupling constants involving protons in the benzene ring attached to the thallium atom are similar to those observed in the phenyl and tolyl dications. However, it is found that in all cases $J_{Tl\text{-}H(5)}$ has a large and approximately constant value, although coupling occurs through 5 bonds. This coupling constant involves a " straight " bond path, and anomalously large H–H coupling constants have been reported for protons that are connected through five bonds by similar conjugated

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[15] Hoffman and Gronowitz, *Arkiv. Kemi*, 1961, **16**, 563.
[16] McConnell, *J. Chem. Phys.*, 1959, **30**, 126.

" straight " bond paths.[8] For example, in quinoline, the coupling[17] between the 4- and 8-protons is 0·8 c./sec. and, on acridine, the analogous H1–H9 coupling[18] is 0·9 c./sec. Inter-ring H–H coupling constants in naphthalene itself have not been observed, but it may be noted that in the A_2B_2 proton resonance of naphthalene, a small coupling constant might not be detected.

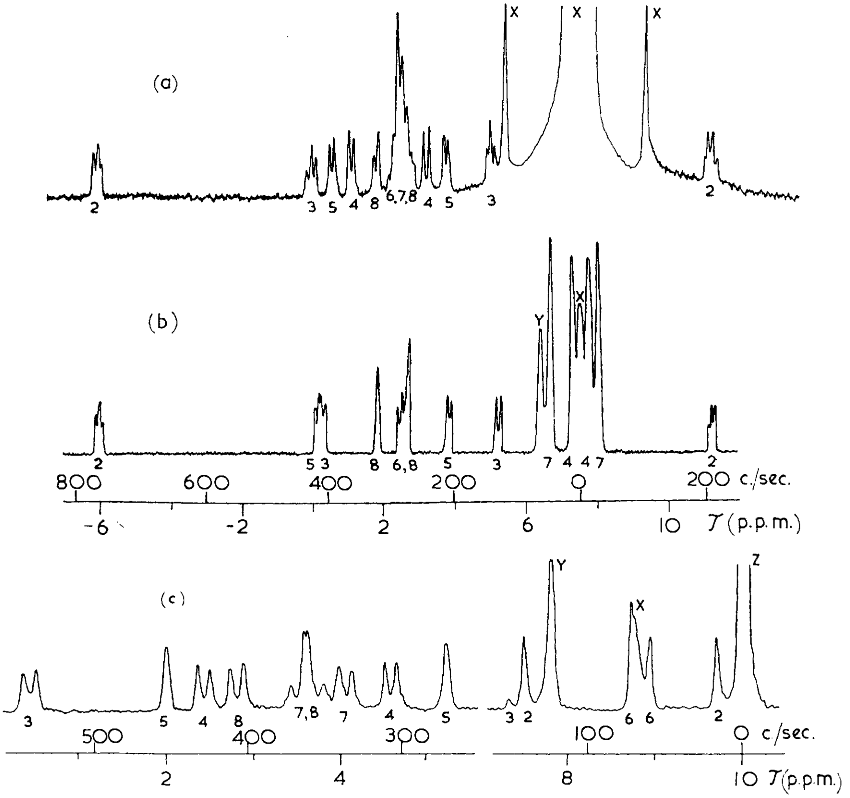

FIG. 1. Proton magnetic resonance spectra.

(a) 1-Naphthylthallium dichloride: X = dimethyl sulphoxide and spinning side-bands. (b) 4,7-Dimethyl-1-naphthylthallium dichloride. (c) 2,6-Dimethyl-1-naphthylthallium dichloride: X = protons in [$^2H_6$]dimethyl sulphoxide; Y = water; Z = tetramethylsilane (internal reference).

Numerals are relative peak areas.

The limited evidence available in these " anomalous " H–H coupling constants suggests that a σ-bond mechanism is involved, since replacing one of the protons by a methyl group leads to an undetectably small coupling constant.[19, 20] A similar conclusion applies to the Tl–H(5) coupling constants. Although an accurate value for $J_{Tl-H(5CH_3)}$ in 5-methyl-1-naphthylthallium dichloride could not be obtained because of the residual proton resonance in [$^2H_6$]dimethyl sulphoxide, it is certainly less than 12 c./sec.

Appreciable Tl–H(8) coupling constants are also observed, and it is significant that in acridine[18] an analogous H(1)–H(8) coupling constant of 0·4 c./sec. has been detected. The smaller Tl–H(6) and Tl–H(7) coupling constants probably largely involve a π-bond

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[17] Anet, *J. Chem. Phys.*, 1960, **32**, 1274.
[18] Kokko and Goldstein, *Spectrochim. Acta*, 1963, **19**, 1119.
[19] Elvidge and Foster, *J.*, 1963, 590.
[20] Hofmann, *Discuss. Faraday Soc.*, 1962, **34**, 157.

mechanism, since comparable coupling constants are obtained when the proton is replaced by a methyl group.

In 9-phenanthrylthallium dichloride, only the Tl–H(10) coupling constant could be measured, and was found to be 1077 c./sec. Thus, the vicinal Tl–H coupling constants increase in the series phenylthallium dichloride (875 c./sec.), 1-naphthylthallium dichloride (948 c./sec.), and 9-phenanthrylthallium dichloride (1077 c./sec.), as does the π-bond order of the intervening C–C bond. Jonathan, Gordon, and Dailey[21] have reported a similar relation between vicinal H–H coupling constants in aromatic hydrocarbons and the π-bond order of the appropriate C–C bond, although the reason for this correlation is not certain.

Vinylthalliums (*Tables* 1 *and* 4).—In vinyl compounds CH_2=CHX, the *trans*-, *cis*-, and geminal H–H coupling constants depend largely upon the electronegativity of X;[8] thus $J_{trans} = +19\ (1—0{\cdot}17\Delta E)$ and $J_{cis} = +11{\cdot}7\ (1—0{\cdot}34\Delta E)$ where ΔE is the difference in electronegativity between X and H. J_{gem} varies from $+7{\cdot}1$ when X = L, to $-3{\cdot}2$ when X = F. The *trans*- and *cis*-Tl–H coupling constants in Tables 1 and 4 are of roughly the expected magnitudes. However, the geminal Tl–H coupling constants are much larger than would be expected from the geminal H–H coupling constants; * this will be discussed later.

TABLE 5.

Tl–H coupling constants in various divinylthallium cations.

	J_{Tl-H}			$J_{Tl-H(CH_3)}$		
Compound	*cis*	*trans*	gem	*cis*	*trans*	gem
$(CH_2$=CH$)_2Tl^+$	$+805 \pm 5$	$+1618 \pm 5$	$+842 \pm 5$			
cis-$(CH_3$·CH=CH$)_2Tl^+$		$+1485 \pm 5$	$+637 \pm 5$	$-94{\cdot}_0$		
trans-$(CH_3$·CH=CH$)_2Tl^+$	$+809 \pm 10$		$+640 \pm 10$		$-47{\cdot}_1$	
trans-$(CH_3$·CH=CH·$CH_3)_2Tl^+$ ...		$+1348 \pm 5$		$-98{\cdot}_0$		398

In methyl-substituted ethylenes it is found that $J_{H-H(cis-CH_3)} = -1{\cdot}7$ to $-1{\cdot}9$, $J_{H-H(trans-CH_3)} = -1{\cdot}2$ to $-1{\cdot}3$, and $J_{H-H(vic-CH_3)}$ $+6{\cdot}0$ c./sec.[23] The negative signs for $J_{H-H(cis-CH_3)}$ and $J_{H-H(trans-CH_3)}$ are in agreement with Karplus's theoretical treatment of the π-contribution to the coupling constants.[24] (Small σ-bond contributions may also be present.) Thus, the Tl–H(CH_3) coupling constants in Table 5 closely parallel the corresponding proton–proton coupling constants.

It was indicated above that strongly electronegative substituents lead to a decrease in the olefinic H–H coupling constants. A similar behaviour is observed for the gem and *cis*-Tl–H coupling constants in the *trans*-(CHCl=CH$)_2Tl^+$ cation. It was not possible to assign uniquely the two Tl–H coupling constants in this compound, since the spectrum consists merely of two AB pairs ($J_{H-H(trans)} = 15{\cdot}0$ c./sec.). However, the possible values are $J_{Tl-H\ cis(gem)}$ 511 c./sec.; $J_{Tl-H\ gem(cis)}$ 453 c./sec.; $J_{Tl-H\ cis(gem)}$ 486 c./sec.; $J_{Tl-H\ gem(cis)}$ 477 c./sec. Whichever assignment is correct, the coupling constants are appreciably smaller than in the divinylthallium cation.

The Alkylthalliums (*Tables* 6 *and* 7 *and* Fig. 2).—In the alkylthalliums, $J_{Tl-H(\beta-CH)}$ is larger than $J_{Tl-H(\alpha-CH)}$ and of an opposite sign. This behaviour is characteristic of alkyl groups bonded to elements in Periods II—VI, with a nuclear spin of $\frac{1}{2}$.[25] Geminal H–H coupling constants in substituted methanes fall between $-9{\cdot}5$ and $-15{\cdot}5$ c./sec., while the vicinal H–H coupling constants in ethyl derivatives, C_2H_5X (equal to $\frac{1}{3}J_{trans} + \frac{2}{3}J_{gauche}$) are *ca.* +7–8 c./sec., and slightly dependent upon the electronegativity of X.[8] Thus, the

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* Similar large geminal metal–proton coupling constants appear in divinylmercury and tetravinyltin.[22]

[21] Jonathan, Gordon, and Dailey, *J. Chem. Phys.*, 1962, **36**, 2443.

[22] Moore and Haffe, *J. Phys. Chem.*, 1961, **65**, 224.

[23] Hoffman and Gronowitz, *Arkiv Kemi*, 1961, **16**, 471.

[24] Karplus, *J. Chem. Phys.*, 1960, **33**, 1842.

[25] Narasimhan and Rogers, *J. Chem. Phys.*, 1961, **34**, 1049; Stafford and Baldeschwieler, *J. Amer. Chem. Soc.*, 1961, **83**, 4473.

TABLE 6.

Tl–H coupling constants in various dialkylthallium cations.

Compound	$J_{\alpha\text{-CH}}$	$J_{\beta\text{-CH}}$	$J_{\gamma\text{-CH}}$
$(CH_3)_2Tl^+$	403		
$(CH_3\cdot CH_2)_2Tl^+$	−340	+628	
$[(CH_3)_2CH]_2Tl^+$	259	574	
$(CH_3\cdot CH_2\cdot CH_2)_2Tl^+$	−341	+469	+20·5
$[(CH_3)_2CH\cdot CH_2]_2Tl^+$	−356	+494	+16·4

Compound	$J_{\alpha\text{-CH}}$	$J_{\beta\text{-CH}}$
$(CH_3\cdot CH_2\cdot CH_2\cdot CH_2)_2Tl^+$	320	452
$(Cyclopentyl)_2Tl^+$	*ca.* 214	*ca.* 214/466
$(CH_3\cdot CH_2\cdot\overset{+}{Tl}\cdot CH_3)$	CH_3 359	
	$CH_3\cdot CH_2$ 399	680

TABLE 7.

Tl–H coupling constants for mixed trialkylthalliums at −60° to −85°.[1,3]

Compound (in CH_2Cl_2)	Me group $J_{Tl-H(CH_3)}$	Et group $J_{Tl-H(CH_2)}$	Et group $J_{Tl-H(CH_3)}$
Me_3Tl...............	251		
Me_2EtTl	223	242	473
$MeEt_2Tl$	187	219	442
Et_3Tl...............		198	396

Compound	$J_{Tl-H(CH_3)}$ in Me_2O	$J_{Tl-H(CH_3)}$ in Me_3N
Me_3Tl	270	270
$Me_2(CH_2{=}CH)Tl$ ...	295	296
$Me(CH_2{=}CH)_2Tl$ ...	317	317

Tl–H(β-CH) coupling constants are *ca.* 65 times the vicinal H–H coupling constant, but the Tl–H(α-CH) coupling constants are considerably less negative than would be expected. This is consistent with the results obtained for the vinylthalliums, where, as discussed above, the geminal coupling constants have anomalously large *positive* values.

In Karplus's valence-bond treatment of geminal H–H coupling constants the signs and magnitude of the calculated values depend in a sensitive manner upon differences between a number of exchange integrals.[12] It is probably for this reason that the calculated sign of the geminal H–H coupling constant in methane was incorrect.[8,26] The apparently anomalous geminal heavy-atom–proton coupling constants may therefore arise from changes in the relative contributions from these exchange integrals, as compared to those in H–H coupling (cf. Klose's calculations on heavy-atom–proton coupling constants).[27]

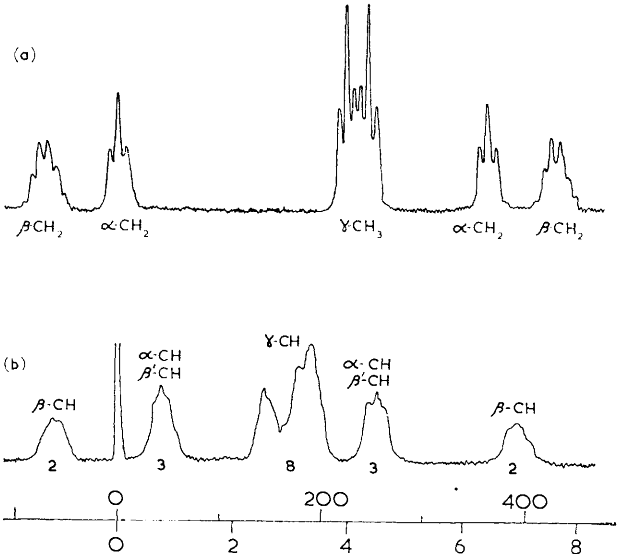

FIG. 2. Proton magnetic resonance spectra.
(a) Di-n-propylthallium sulphate in D_2O. (b) Dicyclopentylthallium sulphate in D_2O.
Internal reference = Bu^tOH.
Numerals are relative peak areas.

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[26] Karplus, *J. Amer. Chem. Soc.*, 1962, **84**, 2458.

[27] Klose, *Ann. Phys.*, 1962, **9**, 262.

The spectrum of the cyclopentylthallium cation is shown in Fig. 2b, and a probable assignment is given. The great width of the lines may be due to molecular motion in the cyclopentane ring.

A few examples of H–H coupling over four bonds in saturated compounds are known. The coupling constants are usually <1 c./sec., are apparently very stereospecific, and both negative and positive signs have been reported.[8,28] The small Tl–H(γ-CH_3) coupling constants in $Pr^n{}_2Tl^+$ and $Bu^i{}_2Tl^+$ are therefore analogous. Similar small ^{199}Hg–H(γ-CH) coupling constants have been found in various compounds of the type CH_3ORHgX;[29] their magnitude was very sensitive to conformational effects.

An unexpected feature is that the numerical value of $J_{Tl-H(CH_3)}$ in $Tl(CH_3)_3$ increases in going from methylene dichloride to dimethyl ether and trimethylamine as solvents (Table 7). Since weak co-ordination of the ether or amine will presumably decrease both the amount of *s*-character in the Tl–C bonds, and also Z_{eff} for the thallium atom, the coupling constants should decrease.

The Mixed Alkylthalliums (*Tables* 6 *and* 7).—In these compounds, the regular changes observed in the Tl–H coupling constants can be interpreted in terms of the electronegativities of the attached groups (cf. Juan and Gutowsky).[10] The more electronegative group will have relatively less *s*-character in its Tl–C bond, and hence the coupling constants involving this group will be less than in the unmixed alkylthallium. Conversely, the coupling constants involving the other group(s) will be increased. The results in Tables 6 and 7 are consistent with an order of electronegativity $CH_2{=}CH > CH_3 > C_2H_5$, which is that expected from the relative inductive effect of these groups in organic compounds.

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[28] Freeman and Bhacca, *J. Chem. Phys.*, 1963, **38**, 1088.

[29] Brownstein, *Discuss. Faraday Soc.*, 1962, **34**, 25.