^{205}Tl–^{1}H Spin–Spin Coupling Constants in the ^{1}H Nuclear Magnetic Resonance Spectra of Substituted Arylthallium Dichlorides

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^{205}Tl–^{1}H Spin–spin coupling constants in various monoarylthallium dichlorides and substituted monoarylthallium dichlorides have been determined in dimethyl sulphoxide solutions in order to compare the couplings with corresponding ^{1}H–^{1}H couplings. It is concluded that there are close resemblances in the behaviour of the ^{205}Tl–^{1}H and the ^{1}H–^{1}H couplings.

THE use of ^{205}Tl–^{1}H spin–spin coupling constants in the determination of the structures of various arylthallium compounds has been discussed recently,[1] and it appears that substituent atoms in the aromatic ring have a marked effect upon the couplings. It was shown in previous work, that whilst the ^{205}Tl–^{1}H

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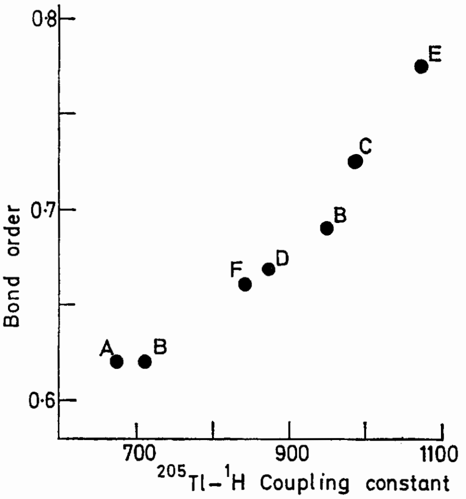
[1] A. McKillop, J. D. Hunt, and E. C. Taylor, *J. Organometallic Chem.*, 1970, **24**, 77.

couplings are numerically very large, their magnitudes can be explained qualitatively on the basis of the Fermi contact interaction, together with the effect of the large effective nuclear charge on the thallium atom.[2] This interpretation is supported by other workers.[3,4] For the compounds $RTlX_2$ (where R is an alkyl, aryl, or vinyl group, X an anion), the $^{205}Tl-^{1}H$ couplings are *ca.* 140 times greater than the corresponding $^{1}H-^{1}H$ couplings, with anions such as perchlorate, sulphate, or nitrate in aqueous solution. Some variation of the couplings occurs with different anions and solvents, though these effects amount to a change in the couplings of less than 10%.[5] Anion and concentration effects can be minimised by using the same anion and solvent when studying a series of different organic groups. A considerable number of $^{1}H-^{1}H$ couplings in a variety of substituted benzenes have now been measured in order to determine some of the factors which may influence these.[6-12] The $^{205}Tl-^{1}H$ couplings in a number of differently substituted $ArTlCl_2$ compounds have thus been measured for comparison with these $^{1}H-^{1}H$ couplings.

DISCUSSION

ortho $^{1}H-^{1}H$ Couplings are considered to be dominated by the σ-electron density of the intervening bonds, and there appears to be a marked dependence upon the bond order; this could be effective by changes in bond lengths and can be viewed as a ' fixation ' of the bonds.[13] For a series of monosubstituted benzenes, the *ortho* $^{1}H-^{1}H$ coupling also correlates fairly well with the electronegativity of the substituent (that is J_{23}, the numbering beginning with the substituent).[7,14] Similar correlations exist for the *meta* and *para* couplings, J_{24} and J_{26}.[12]

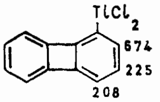
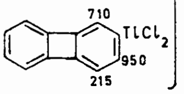
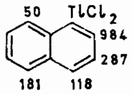
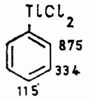
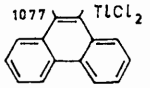
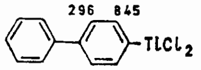


Plot of bond order *vs.* $^{205}Tl-^{1}H$ (*ortho*) couplings, values corresponding to those in Table 1

If the *ortho* $^{205}Tl-^{1}H$ coupling in various aromatic thallium compounds is plotted against the bond order, estimated from simple MO theory for the parent hydrocarbons,[15] a nearly linear correlation is observed (see Figure). The corresponding bond lengths for the free hydrocarbons, $^{1}H-^{1}H$ coupling constants for these, and the other $^{205}Tl-^{1}H$ couplings are shown in Table 1. The Figure may be extrapolated (approximately) to the *cis*-coupling found in β-styrylthallium dichloride (*ca.* 1600

TABLE 1

$J(^{205}Tl-^{1}H)$ and $J(^{1}H-^{1}H)$ and bond lengths

Tl-compound		Free hydrocarbon	
		Bond length (Å)	$^{1}H-^{1}H$ coupling (Hz)
A		1,2 1·42[a] 2,3 1·35[a]	J_{12} 7·1[b] J_{23} 8·1[b] J_{13} 0·8[b] J_{14} 1·0[b]
B			
C[c]		1,2 1·361	J_{12} 8·2[b] * J_{13} 1·3[b] J_{14} 0·5[b]
D[c]		1,2 1·39[d]	J_{12} 7·50[e] J_{13} 1·35[e] J_{14} 0·66[e]
E[c]			$J_{9,10}$ 9·3 in 1-phenylphenanthroline[f]
F[c]		1,2 1·39[d]	

[a] From T. C. W. Mak and J. Trotter, *J. Chem. Soc.*, 1962, 1. [b] From A. R. Katritzky and R. E. Reavill, *Rec. Trav. chim.*, 1964, **83**, 1230. [c] From J. P. Maher and D. F. Evans, *J. Chem. Soc.*, 1965, 637. [d] From Chemical Society Special Publications Nos. 11 and 18, ' Interatomic Distances.' [e] From S. Castellano, R. Kostelnik, and C. Sun, *Tetrahedron Letters*, 1967, 5211. [f] From K. D. Bartle, P. M. G. Bavin, and D. W. Jones, *Org. Magnetic Resonance*, 1970, **2**, 259.

* Inter-ring $^{1}H-^{1}H$ coupling constants J_{15} 0·85 Hz, J_{18} −0·45 Hz have recently been detected in naphthalene, R. W. Crecely and J. H. Goldstein, *Org. Magnetic Resonance*, 1970, **2**, 613.

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[2] J. P. Maher and D. F. Evans, *J. Chem. Soc.*, 1965, 637.

[3] J. V. Hatton, *J. Chem. Phys.*, 1964, **40**, 933.

[4] K. Hildenbrand and H. Dreeskamp, *Z. phys. Chem.* (*Frankfurt*), 1970, **69**, 171.

[5] G. D. Shier, Ph.D. Thesis, University of Illinois, 1964 (University Microfilms No. 65–3672).

[6] P. F. Cox, *J. Amer. Chem. Soc.*, 1963, **85**, 380.

[7] S. Castellano and C. Sun, *J. Amer. Chem. Soc.*, 1966, **88**, 4742.

[8] B. Rischler, *Z. Naturforsch.*, 1965, **20***A*, 888.

[9] J. M. Read, jun., R. W. Crecely, R. S. Butler, J. E. Loemaker, and J. H. Goldstein, *Tetrahedron Letters*, 1968, 1215.

[10] T. Schaefer, G. Kotowycz, H. M. Hutton, and J. W. S. Lee, *Canad. J. Chem.*, 1968, **46**, 2531.

[11] (*a*) S. Castellano, R. Kostelnik, and C. Sun, *Tetrahedron Letters*, 1967, 4635; (*b*) *ibid.*, 1967, 5205; (*c*) *ibid.*, 1967, 5211.

[12] K. Hayamiza and O. Yamamoto, *J. Mol. Spectroscopy*, 1968, **25**, 422.

[13] N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, 1962, **36**, 2443.

[14] R. R. Fraser, *Canad. J. Chem.*, 1966, **44**, 2737.

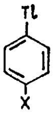
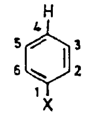
[15] K. Higasi, H. Baba, and A. Rembaum, ' Quantum Organic Chemistry,' Interscience, Wiley, New York, 1965.

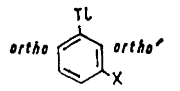
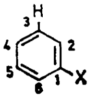
Hz) and the *cis*-coupling in vinylthallium dichloride (1650 Hz), both with bond orders of *ca.* 1.[16]

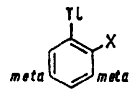
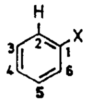
That the thallium atom does have some effect on the ring structure (and cannot just be regarded as a ' super-proton '!) can be seen from the difference in the ^{205}Tl–^{1}H couplings across the 1,2-position in α-biphenylenylthallium dichloride and β-biphenylenylthallium dichloride. The similar size of the ^{1}H–^{1}H couplings J_{13} and J_{14} in biphenylene correlates well with the couplings in the thallium derivatives, since the *meta* and *para* ^{205}Tl–^{1}H couplings are also of similar size.

TABLE 2

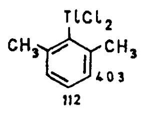
The relative sizes of the ^{205}Tl–^{1}H and ^{1}H–^{1}H coupling constants [a] in various substituted benzenes expressed as a fraction of the couplings in phenylthallium dichloride [b] and in benzene * respectively

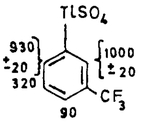
	X	F	Cl	Br	OCH_3	CF_3	CHO	CO_2H	C_6H_5	CH_3
(a) *para*-substituent										
	*ortho*	0·95	0·92	0·93	0·95	0·96	0·93	0·94	0·96	0·98
	meta	0·71	0·73	0·76	0·78	0·79	0·87	0·88	0·89	0·94
	3,4	0·99	1·00	0·99	0·98	1·01				1·01
	2,4	0·76	0·82	0·81	0·76	0·94				1·00

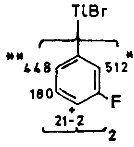
(b) *meta*-substituent	X	Cl	CF_3	NO_2	CO_2H	CH_3
	*ortho*	0·92	0·98	0·92	0·95	1·00
	ortho'	1·00	1·05	1·07	1·01	1·04
	meta	1·09	0·88	0·96	0·93	1·10
	para	0·55	0·73	0·50	0·79	0·87
	3,4	1·00	1·01	0·99		1·01
	2,3	1·07	1·06	1·11		1·01
	3,5	1·24	0·96	1·07		1·13
	3,6	0·76	0·94	0·77		1·00

(c) *ortho*-substituent	X	OCH_3	NO_2	CF_3	CH_3	C_2H_5
	*ortho*	1·10	0·97	0·91 ± 0·02	1·02	1·04
	meta	0·75	0·61	0·64	0·90	0·90
	meta	1·40	1·22	1·13	1·36	1·36
	para	0·56	0·59	0·76	0·98	1·02
	2,3	1·10	1·11	1·06	1·01	
	2,4	0·76	0·85	0·94	1·00	
	2,6	1·99	1·75	1·46		
	2,5	0·67	0·77	0·92		

In addition to these the following were measured in deuteriodimethyl sulphoxide:







* The ^{1}H–^{1}H coupling data are taken from S. Castellano and C. Sun, *J. Amer. Chem. Soc.*, 1966, **88**, 4742; T. Schaefer, G. Kotowycz, H. M. Hutton, and J. W. S. Lee, *Canad. J. Chem.*, 1968, **46**, 2531; R. J. Kostelnik, M. P. Williamson, D. E. Wisnosky, and S. M. Castellano, *ibid.*, 1969, **47**, 3313, and are normalised to the relevant couplings in benzene (Table 1). The errors are considered to be *ortho* ± 0·02; *meta* ± 0·10; *para* ± 0·20. ** These cannot be distinguished from the spectra but are assigned on the basis of the couplings in the Cl derivative Table 2b.

[a] The ^{205}Tl–^{1}H couplings are accurate to ±0·01, these are normalised to the couplings of phenylthallium dichloride shown in Table 1. [b] From J. P. Maher and D. F. Evans, *J. Chem. Soc.*, 1965, 637.

Table 2a shows the relative sizes of the ^{205}Tl–^{1}H couplings for a series of *para*-substituted arylthallium dichlorides. These are expressed for convenience as a proportion of the coupling constants in the ' parent ' compound phenylthallium dichloride. The *meta* ^{205}Tl–^{1}H coupling shows the largest effect; there being a tendency for the coupling to decrease as the electronegativity of the substituent increases. This correlates

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[16] J. P. Maher, Ph.D. Thesis, University of London, 1963.

to a slight extent with the effect of the substituent upon J_{24} in the monosubstituted hydrocarbon. The effect upon the *ortho* ^{205}Tl–^{1}H couplings is much less clear and much smaller, as is the case for the ^{1}H–^{1}H coupling, J_{34}, in monosubstituted benzenes.[9,10] In both the ^{1}H–^{1}H and the ^{205}Tl–^{1}H couplings the percentage size and direction of the change (a decrease) is similar.

Tables 2b and c show more data for the ^{205}Tl–^{1}H couplings in various *ortho*- and *meta*-substituted arylthallium dichlorides. The same general point seems to apply, namely that the percentage change in the ^{1}H–^{1}H coupling is mirrored to some extent by the corresponding ^{205}Tl–^{1}H coupling. This point is again illustrated in the Table by including the (normalised) values for ^{1}H–^{1}H couplings. The rather large uncertainty in the latter couplings precludes further discussion of the ratios.

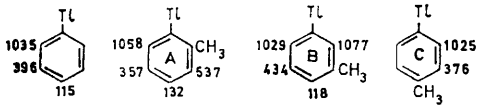
As with the ^{1}H–^{1}H couplings the ^{205}Tl–^{1}H couplings show the greatest changes from the parent hydrocarbon and phenylthallium dichloride when the coupling occurs across the substituent, and also when the coupling occurs to a proton situated close to a substituent (*cf.* J_{24} and the *meta* ^{205}Tl–^{1}H coupling in the *para*-substituted phenylthallium dichlorides). It has been suggested that substituent effects on couplings in substituted benzenes are relatively short range,[10] and that these represent changes in the σ-bond frame work arising from either inductive or bond order effects.[6]

Changes in the symmetry of the π-molecular orbitals might also be reflected in the couplings; these would probably be more significant for the *meta*- and *para*-couplings, than for the *ortho*-couplings.[17] The situation is not very clear since it is difficult to disentangle σ and π contributions to the couplings. However, comparing the ^{205}Tl–^{1}H coupling to a proton with that to a methyl group in the same position might be helpful in this latter respect.[2,18,19] The ethyl group in 2-ethylphenylthallium dichloride has a very similar effect on the ring ^{205}Tl–^{1}H couplings to that of the methyl group in 2-methylphenylthallium dichloride. The lack of any coupling to the CH_3 group in the former compound is consistent with the idea that the coupling mechanism to the CH_2 is dominated by a σ–π configuration interaction.[19]

Several papers have proposed additivity schemes for predicting ring-proton coupling constants in variously substituted benzenes.[8-10,11c] Evidence has been found for additivity effects in other couplings.[20] With the data available so far it is only possible to test for additivity relationships in the various methyl-substituted phenylthallium compounds. Using the ^{205}Tl–^{1}H couplings shown in Table 3, predictions about the couplings in di- and tri-methylphenylthallium compounds can be made. The data are not good enough to demonstrate conclusively that an additivity relation occurs, but the couplings show fair agreement, and we may conclude that an additivity relation is applicable.

TABLE 3

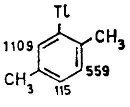
Test for additivity effects



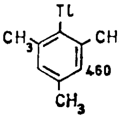
ΔJ_o^{A} + 23	ΔJ_o^{B} − 6	ΔJ_o^{C} − 10
$\Delta J_{m'}^{A}$ − 39	$\Delta J_{o'}^{B}$ + 42	ΔJ_m^{C} − 20
$\Delta J_{m'}^{A}$ + 141	ΔJ_m^{B} + 38	
ΔJ_p^{A} + 17	ΔJ_p^{B} + 3	

The couplings in A and C were estimated from those in the (Ar–Tl^{2+}) SO_4^{2-} couplings previously measured in D_2O (J. P. Maher, Ph.D. Thesis, University of London, 1963) by assuming a multiplication factor of × 1·09 for the Ar–Tl $(OCOCF_3)_2$ compound. This gives the couplings to within *ca.* ±2%. The other couplings are all taken from A. McKillop, J. D. Hunt, and E. C. Taylor, *J. Organometallic Chem.*, 1970, **24**, 77.

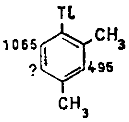
Experimental Calculated



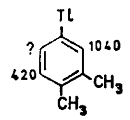
$$J_o = \Delta J_o^{A} + \Delta J_{o'}^{B} + J_{ortho} = 1100$$
$$J_m = \Delta J_{m'}^{A} + \Delta J_m^{B} + J_{meta} = 575$$
$$J_p = \Delta J_p^{A} + \Delta J_p^{B} + J_{para} = 135$$



$$J_m = \Delta J_m^{A} + \Delta J_{m'}^{A} + \Delta J_m^{C} + J_{meta} = 478$$



$$J_o = \Delta J_o^{A} + \Delta J_o^{C} + J_{ortho} = 1048$$
$$J_m = \Delta J_m^{A} + \Delta J_{m'}^{C} + J_{meta} = 337$$
$$J_{m'} = \Delta J_m^{A} + \Delta J_{m'}^{A} + J_{meta} = 498$$



$$J_o = \Delta J_{o'}^{B} + \Delta J_o^{C} + J_{ortho} = 1057$$
$$J_{o'} = \Delta J_o^{B} + \Delta J_o^{C} + J_{ortho} = 1019$$
$$J_m = \Delta J_m^{B} + \Delta J_m^{C} + J_{meta} = 414$$

The last two compounds as reported by McKillop *et al.*: $[2,4\text{-}(CH_3)_2C_6H_3]Tl(OCOCF_3)_2$, and $[3,4\text{-}(CH_3)_2C_6H_3]Tl(OCOCF_3)_2$ have ambiguous values for the ^{205}Tl–^{1}H (*meta*) and ^{205}Tl–^{1}H (*ortho*) couplings, only one being reported in each case, whereas two different values would be expected. This unfortunately precludes further comparison of any additivity effect.

This preliminary study does indicate that the ^{205}Tl–^{1}H couplings in the arylthallium compounds behave in a like manner to ^{1}H–^{1}H couplings in benzenes. This finding agrees with previous ideas propounded on ^{205}Tl–^{1}H couplings.

A further study of the ^{205}Tl–^{1}H couplings in substituted aromatic compounds would be worthwhile in that the couplings are considerably longer than the ^{1}H–^{1}H couplings in benzenes and consequently much easier to measure, making the study of substituent effects

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[17] H. M. McConnell, *J. Mol. Spectroscopy*, 1957, **1**, 11; *J. Chem. Phys.*, 1959, **30**, 126.

[18] R. A. Hoffman and S. Gronowitz, *Arkiv Kemi*, 1961, **16**, 563.

[19] C. N. Banwell and M. Sheppard, *Discuss. Faraday Soc.*, 1962, **34**, 115.

[20] T. Vladimiroff, *Diss. Abs.*, 1968, **28***B* (8), 3248.

easier. The ^{205}Tl–^{1}H couplings also provide a valuable method of identification of the site of ' thalliation ', thus additivity relationships, if they can be demonstrated more conclusively, would be very useful for compound identification.

EXPERIMENTAL

The monoarylthallium compounds were prepared *via* the corresponding aryl boronic acids (for which satisfactory analyses were obtained), by reaction with thallium(III) chloride. The ^{1}H n.m.r. spectra of the crude products were measured in [^{2}H$_6$]dimethyl sulphoxide solution on Varian A-60 and HA-100 spectrometers. The coupling constants were virtually independent of concentration for the moderately (10—20%) concentrated solutions used. They are estimated to be accurate to ±1%.

We wish to thank Dr. D. F. Evans and Dr. J. F. W. McOmie for assistance with the preparation and provision of compounds described in this work.

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