

## <sup>13</sup>C NMR OF ALKYL-SUBSTITUTED ARYLTHALLIUM TRIFLUORO-ACETATES

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### Summary

<sup>13</sup>C chemical shifts and <sup>13</sup>C—<sup>205</sup>Tl spin—spin coupling constants over two to six bonds (including most of the signs) are reported for alkyl-substituted arylthallium trifluoroacetates. After a detailed description of the method of signal assignment, substituent effects on chemical shifts and coupling constants are derived. The dependence of <sup>n</sup>J(<sup>13</sup>C, <sup>205</sup>Tl) on the conformation of alkyl side-chains *para* to the Tl(OCOCF<sub>3</sub>)<sub>2</sub> group is shown.

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### Introduction

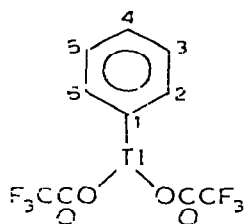
There are few reports in the literature on <sup>13</sup>C NMR spectra of organo-thallium compounds; the first, by Hildenbrand and Dreeskamp on trimethylthallium and dimethylthallium bromide, appeared in 1970 [1]. Abraham's group reported <sup>13</sup>C—<sup>205</sup>Tl spin—spin coupling constants in porphyrin derivatives with Tl<sup>III</sup> as the central metal atom [2]. Kitching, Praeger, Moore, Doddrell and Adcock [3] recently published <sup>13</sup>C NMR data for phenylthallium trifluoroacetate and four of its methyl-substituted derivatives, which are markedly in conflict with our results [4].

Our investigations are now extended to arylthallium compounds with higher alkyl sidechains in order to get some insight into the nature of long-range carbon—thallium coupling. Substituent effects on <sup>n</sup>J(<sup>13</sup>C, <sup>205</sup>Tl), where *n* = 2—5, and on <sup>13</sup>C chemical shifts are also discussed. Moreover, detailed arguments for the assignment of resonances to specific carbons are given to show that the results of ref. 4 are correct. <sup>1</sup>H NMR results are included as far as they are relevant to the present study.

### Results and discussion

<sup>13</sup>C NMR spectra were obtained for dimethyl sulfoxide-*d*<sub>6</sub> solutions of

compounds I to XI. The chemical shifts are given in Table 1 together with the substituent-induced shift, i.e. the difference in chemical shifts between the thallium derivative and the parent hydrocarbon. Hydrocarbon shifts were measured for 40% (v/v) solutions in DMSO- $d_6$ , i.e. under approximately the same experimental conditions, and are not given here.



(I)

- (II) 4-Me, (III) 4-Et, (IV) 4-*i*-Pr, (V) 4-*t*-Bu;  
 (VI) 4-*n*-Pr, (VII) 2,4-Me<sub>2</sub>, (VIII) 2,5-Me<sub>2</sub>,  
 (IX) 3,4-Me<sub>2</sub>, (X) 2,4,6-Me<sub>3</sub>; (XI) 2,4,6-Et<sub>3</sub>

Table 2 shows the  $^{13}\text{C}$ - $^{205}\text{Tl}$  coupling constants over two to six bonds. The one-bond couplings range from 9 to 10 kHz [3]; they were not determined because it proved difficult to obtain a good enough signal-to-noise ratio to identify unequivocally the signals, which are presumably rather broad [3] and weak. The signs of  $J(\text{C}, \text{Tl})$  are given explicitly in those cases where they were determined. Signs deduced from analogous compounds are given in brackets.

Before a discussion of these results is undertaken, it is essential to demonstrate that the assignment of the signals to the specific carbons is unambiguous, for the discrepancies between refs. 3 and 4 apparently result from wrong assignments in the former.

In the aromatic region, compound II shows six signals, two of which are only half as intense as the remainder and therefore are readily assigned to C-4. Thus the remaining signals at 2732, 3089, 3651 and 3816 Hz downfield from TMS (at 25.16 MHz) belong to C-2 and C-3. Those at 2732 and 3816 Hz are broader and slightly less intense than the others. On the inside these two signals show almost resolved splittings at half height which are due to the  $^{203}\text{Tl}$  isotope. Therefore they correspond to the same carbon and give for it  $\delta$  130.2 ppm and  $J(\text{C}, ^{205}\text{Tl})$  1084 Hz.  $J(\text{C}, ^{203}\text{Tl})$  is 1074 Hz from which the ratio of the  $^{205}\text{Tl}/^{203}\text{Tl}$  magnetic moments is calculated to be 1.0093 (theoretical value 1.0097). The signals at 3089 and 3651 Hz give  $\delta$  133.9 ppm and  $J(\text{C}, \text{Tl})$  562 Hz. The fact that the shift of a signal from a carbon *meta* to a substituent is always least affected leads to the assignment C-2  $\delta$  133.9 ppm,  $J$  562 Hz and C-3  $\delta$  130.2 ppm,  $J$  1084 Hz. Pairing the doublets in the wrong order leads approximately to the results of ref. 3.

Evidence for the correct assignment can be obtained independently for the other compounds, e.g. IX. The aromatic region contains ten signals, labelled A to J, for C-2 to C-6 which are all non-equivalent by lack of symmetry. The frequencies of these signals, their multiplicity and residual  $^1J(\text{C}, \text{H})$  couplings in the single-frequency off-resonance  $^1\text{H}$ -decoupled (SFORD) spectrum are listed in Table 3. Signals A, D, F and I belong to quarternary carbons, viz. C-3

(continued on p. 323)

TABLE 1

 $^{13}\text{C}$  CHEMICAL SHIFTS ( $\delta$ ) OF ALKYL-SUBSTITUTED ARYLTHALLIUM TRIFLUOROACETATES AND SUBSTITUENT-INDUCED SHIFTS<sup>a, b, c</sup>

Compound	C-2	C-3	C-4	C-5	C-6	C-4 $\alpha$	C-4 $\beta$	Other C
I <sup>d</sup>	134.4 (5.9)	129.8 (1.3)	130.1 (1.6)	129.8 (1.3)	134.1 (5.9)			
II <sup>c</sup>	133.9 (5.6)	130.2 (1.0)	139.8 (2.2)	130.2 (1.0)	133.9 (5.6)	20.8 (- 0.4)		
III	131.1 (5.6)	128.9 (1.0)	145.9 (1.9)	128.9 (1.0)	134.1 (5.6)	28.1 (- 0.6)	15.5 (- 0.2)	
IV	134.6 (6.2)	127.9 (1.5)	151.2 (2.6)	127.9 (1.5)	134.6 (6.2)	33.9 (0.0)	24.0 (0.0)	
V	133.9 (5.8)	126.5 (1.4)	152.8 (2.2)	126.5 (1.4)	133.9 (5.8)	34.5 (0.1)	31.1 (- 0.2)	
VI	134.1 (5.7)	129.6 (1.1)	144.5 (2.1)	129.6 (1.1)	134.1 (5.7)	37.1 (- 0.8)	24.3 (- 0.2)	13.6 (C-4 $\gamma$ ) (- 0.2)
VII	141.5 (4.0)	131.1 (1.5)	139.9 (2.5)	127.2 (1.0)	134.4 (6.1)	20.6 ( 0.5)	24.0 (2.8)	
VIII	136.4 (3.9)	140.4 (1.4)	130.7 (1.7)	135.8 (1.3)	134.7 (5.7)		23.6 (2.8)	20.7 (- 0.1) (C-5 $\alpha$ )
IX	134.6 (5.0)	137.7 (1.5)	138.5 (2.3)	130.4 (0.8)	131.5 (5.6)	19.2 (- 0.2)	19.5 (0.1)	
X	141.6 (4.3)	128.9 (1.9)	140.2 (2.9)	128.9 (1.9)	141.6 (4.3)	20.5 (- 0.5)	24.2 (3.2)	
XI	147.7 (3.7)	126.8 (1.9)	147.0 (3.0)	126.8 (1.9)	147.7 (3.7)	28.3 (- 0.3)	15.7 (- 0.3)	32.4 (3.8) (C-2 $\alpha$ ) (C-2 $\beta$ )

<sup>a</sup> Average values for CF<sub>3</sub>CO<sub>2</sub> substituents. CF<sub>3</sub>  $\delta$  118.3 ppm, J(C, F) 291.5 Hz; CO  $\delta$  159.9 ppm, J(C, F) 35.9 Hz. <sup>b</sup> Concentrated solutions in DMSO-*d*<sub>6</sub>. <sup>c</sup> Chemical shifts referred to internal TMS. <sup>d</sup> Substituent-induced shifts (see text) in brackets. <sup>e</sup> Compound also measured in CD<sub>3</sub>OD/TFA (6/4);  $\delta$  2 135.7,  $\delta$  3 131.2,  $\delta$  4 132.1 ppm. <sup>f</sup> Compound also measured in THF/acetone-*d*<sub>6</sub> (7/3);  $\delta$  2 134.9,  $\delta$  3 131.4 ppm.

TABLE 2  
SPIN-SPIN COUPLING CONSTANTS BETWEEN  $^{205}\text{Tl}$  AND  $^{13}\text{C}$  (CARBON INDICATED)

Compound	C-2	C-3	C-4	C-5	C-6	C-4 $\alpha$	C-1 $\beta$	Other C
I <sup>a</sup>	(+)500	(+)1010	(-)185	(+)1010	(+)500			
II <sup>b</sup>	(+)562	(+)1084	(-)209	(+)1084	(+)562	114		
III	(+)556	(+)1066	(-)199	(+)1066	(+)556	99	48	
IV	(+)563	(+)1072	(-)206	(+)1072	(+)563	91	29	
V	(+)560	(+)1062	(-)211	(+)1062	(+)560	79	23	
VI	(+)562	(+)1075	(-)204	(+)1075	(+)562	94	47	(C-4 $\gamma$ ) (C-2 $\alpha$ )
VII	+ 567	+ 1017	- 191	+ 1048	+ 505	112		444 (C-2 $\alpha$ )
VIII	+ 520	+ 1047	- 196	+ 1015	+ 491			446 (C-2 $\alpha$ )
IX	+ 552	+ 1071	- 217	+ 1101	+ 515	92		76 (C-3 $\alpha$ )
X	(+)509	(+) 996	(-)174	(+) 996	(+)509	115		454 (C-2 $\alpha$ )
XI	(+)557	(+) 987	(-)173	(+) 987	(+)557	104	38 <sup>c</sup>	437 (C-2 $\alpha$ ) <sup>d</sup>

<sup>a</sup> Very broad lines due to association; thus, couplings are accurate to only  $\pm 15$  Hz. Compound also measured in  $\text{CD}_3\text{OD/TFA}$  (6/4), couplings: C-2 547 Hz, C-3 1047 Hz. <sup>b</sup> Compound also measured in  $\text{THF/acetone-}d_6$  (7/3), couplings: C-2 589 Hz, C-3 1065 Hz, C-4 1065 Hz, C-5 10 Hz due to overlap with C-2 $\beta$  signal. <sup>c</sup>  $\pm 3$  Hz due to overlap with solvent signal.

TABLE 3  
ASSIGNMENT FOR CARBONS C-2 TO C-6 OF COMPOUND IX

Signal	Frequency <sup>a</sup>	Multiplicity <sup>b</sup>	$J_r$ <sup>c</sup>	$\Delta\nu$ <sup>d</sup>	$J_r/\sqrt{J_0^2 - J_r^2}$ <sup>e</sup>	Assignment
A	3999	s	0			C-3
B	3831	d	72	1325	0.50	C-5
C	3661	d	86	1640	0.64	C-2
D	3593	s	0			C-4
E	3565	d	85	1626	0.63	C-6
F	3376	s	0			C-4
G	3109	d	37	614	0.24	C-2
H	3050	d	39	618	0.25	C-6
I	2928	s	0			C-3
J	2730	d	53	913	0.35	C-5

<sup>a</sup> In Hz from TMS at 25.16 MHz. <sup>b</sup> In SFORD spectrum s = singlet, d = doublet. <sup>c</sup> Residual <sup>1</sup>J(C, H) in Hz; decoupler frequency 400 Hz upfield from TMS. <sup>d</sup> Transition frequency of corresponding protons relative to decoupler frequency. <sup>e</sup> Assuming  $J_0 = 160$  Hz.

and C-4, as they remain singlets in the SFORD spectrum. Tl-coupling to C-4 is expected to be of the order of 200 Hz, and coupling to C-3 should be ca. 1000 Hz by analogy with compound II; thus, lines D and F represent the C-4 transitions, yielding  $\delta_4$  138.5 ppm,  $J$  217 Hz, and A and I the C-3 transitions:  $\delta_3$  137.7 ppm,  $J$  1071 Hz. Again lines A and I are broader than D and F because of the <sup>203</sup>Tl satellites which are not resolved here. The remaining signals which are all doublets in the SFORD spectrum are due to C-2, C-5 and C-6. Here the residual <sup>1</sup>J(C, H) couplings,  $J_r$ , facilitate the assignment. For their interpretation the <sup>1</sup>H spectrum has to be considered. At the same magnetic field strength, the transitions of <sup>1</sup>H-2 occur at 1240 and 214 Hz from TMS [due to  $\delta$ (H-2) 7.27 ppm and  $J$ (Tl, H) 1026 Hz], <sup>1</sup>H-5 at 925 and 513 Hz [ $\delta$ (H-5) 7.19 ppm,  $J$ (Tl, H) 412 Hz] and <sup>1</sup>H-6 at 1226 and 218 Hz [ $\delta$ (H-6) 7.22 ppm,  $J$ (Tl, H) 1008 Hz]. As the decoupler frequency was chosen to be -400 Hz from TMS, the differences  $\Delta\nu$  between proton transitions and decoupler frequency are those shown in Table 3.

Pachler [5] has derived an equation that relates  $\Delta\nu$  and  $J_r$ , viz.:

$$\Delta\nu = \gamma H_2 J_r / 2\pi \sqrt{J_0^2 - J_r^2}$$

which holds if the decoupling power level  $\gamma H_2 / 2\pi$  is large compared to  $0.5(J_0 - J_r)$  where  $J_0$  is the true C,H-coupling constant. As this condition is fulfilled in the present experiments, correct assignment should yield a straight line if  $\Delta\nu$  is plotted vs.  $J_r/\sqrt{J_0^2 - J_r^2}$ . With the assignment given below this is in fact the case. From there it follows that lines B and J represent transitions of C-5. C, E, G and H then belong to C-2 and C-6. Consideration of the shift differences between C-3 and C-5 in *o*-xylene ( $\delta_3 - \delta_5 = 3.7$  ppm), which correspond to C-2 and C-6 in IX, makes the assignment of lines C and G to C-2 and of E and H to C-6 very probable. This results in  $\delta_2$  134.6 ppm,  $J$  552 Hz and  $\delta_6$  131.5 ppm,  $J$  515 Hz. The other possible assignment, viz. C and H to C-2 and E and G to C-6, would give  $\delta_2$  133.4 ppm,  $J$  611 Hz and  $\delta_6$  132.6 ppm,  $J$  456 Hz. Because of the small shift difference and the large difference in coupling constants, this alternative is highly unlikely.

The fact that the Tl,H coupling constants are so large (<sup>o</sup> $J$  1000, <sup>m</sup> $J$  400 and <sup>p</sup> $J$  100 Hz) allows easy determination of the relative signs of <sup>n</sup> $J$ (Tl, C) and <sup>n+1</sup> $J$ (Tl, H)

[6]. Consider the proton transitions of H-2 (at 1640 and 614 Hz downfield from the decoupler frequency) and the transitions of C-2 (lines C and G) in IX. In the SFORD  $^{13}\text{C}$  spectrum, line C has  $J_c$  of 86 Hz, whereas line G is split by 37 Hz. Hence the low field  $^{13}\text{C}$  transition (C) is related to the low-field  $^1\text{H}$  transition and the high-field  $^{13}\text{C}$  line (G) to the high-field  $^1\text{H}$  line. Therefore  $^3J(\text{Tl, H-ortho})$  and  $^2J(\text{Tl, C-ortho})$  have the same sign. Likewise the SFORD spectra of VII, VIII, IX gave  $^4J(\text{Tl, H-metal})/-^3J(\text{Tl, C-meta}) > 0$ ,  $^5J(\text{Tl, H-para})/^3J(\text{Tl, C-para}) < 0$ ,  $^4J(\text{Tl, CH}_3\text{-ortho})/^3J(\text{Tl, C-ortho}) < 0$ ,  $^5J(\text{Tl, CH}_3\text{-meta})/^3J(\text{Tl, C-ortho}) > 0$  and  $^6J(\text{Tl, CH}_3\text{-para})/^5J(\text{Tl, C-ortho}) < 0$ . As the coupling constants between Tl and the *o*-, *m*- and *p*-protons in diphenyl-thallium chloride have been shown to be positive [1], it follows that the couplings to the *o*-, *m*- and *p*-carbons are positive, positive and negative, respectively. Since the signs of the couplings from the thallium to the *o*-, *m*- and *p*-CH<sub>3</sub>-protons are not definitely known, the signs of  $^3J(\text{Tl, C-CH}_3)$ ,  $^4J(\text{Tl, m-CH}_3)$  and  $^5J(\text{Tl, p-CH}_3)$  cannot be derived with absolute certainty. However, Hoffman's "methyl group replacement technique" [7] suggests that, if  $^5J(\text{Tl, p-H})$  is positive, then, given the coupling is mainly transmitted through the aromatic  $\pi$ -system,  $^6J(\text{Tl, p-CH}_3)$  should be negative. Thus  $^5J(\text{Tl, p-CH}_3)$  is probably positive. The findings of Maher et al. [8, 9] that Tl,H couplings in aromatic systems are larger than analogous H,H-couplings by a constant factor suggests that  $J(\text{Tl, CH}_3)/J(\text{H, CH}_3) > 0$  also for *o*-, *m*- and *p*-methyl protons. If this is so, then the 3-, 4- and 5-bond couplings between Tl and the *o*-, *m*- and *p*-carbons of the methyl groups are all positive.

After establishing the correct assignment we can now discuss the parameters obtained. The chemical shifts induced by introduction of the  $\text{Tl}(\text{OCOFCF}_3)_2$  group into the hydrocarbons are  $5.0 \pm 1.3$  ppm for the *ortho*-carbons. As is evident from Tab. 1 these induced shifts can be divided into two groups: signals from unsubstituted *o*-carbons are shifted by  $5.9 \pm 0.3$  ppm to low field and those from *o*-carbons with an alkyl-substituent are affected by only  $4.0 \pm 0.3$  ppm and thus are less susceptible to influences from the Tl substituent. Signals from *meta*-carbons are also shifted downfield, although much less so. The range of these shifts is 0.8–1.9 ppm. Signals from *m*-carbons with one *o*-methyl or *o*-ethyl group lie at the lower and those having two *o*-alkyl groups at the upper end of this range. The substituent-induced shifts for the *para*-position are again positive, yet more so than for the *meta*-positions. They range from 1.6 to 3.0 ppm. Here, quarternary carbons are affected more than tertiary ones. Strong downfield shifts are also observed for *o*-methyl carbons (2.8–3.8 ppm), whereas *m*-substituents suffer little influence, and the signals from both  $\alpha$ - and  $\beta$ -carbons of *p*-alkyl groups are generally shifted upfield by up to 0.6 ppm.

The Tl,C-coupling constants fall into characteristic ranges, depending on the number of intervening bonds. For the aromatic carbons one finds  $^2J + 460 - +570$  Hz,  $^3J + 990 - +1100$  Hz and  $^4J - 170 - 220$  Hz. There are substantial substituent effects; e.g. in the unsymmetrical compounds  $^2J$  is larger for quarternary than for tertiary carbons, and larger for tertiary carbons with an *o*-substituent than for those without.  $^3J$ , on the contrary, is smaller where a quarternary carbon is involved. For a generalization of these effects, a larger number of compounds would have to be examined. Couplings between Tl and  $\alpha$ -alkyl carbons range from 437 to 454 Hz for *ortho*-, from 76 to 92 Hz for *meta*- and from 79 to 115 Hz for *para*-substituents. It is noteworthy that in the *o*-xylene derivative IX  $^4J(\text{Tl, m-CH}_3)$  and  $^5J(\text{Tl, p-CH}_3)$  are distinctly smaller than in similar compounds where no interference of *o*-substituents is possible. As for the size of  $^5J(\text{Tl, p-C}_\alpha)$ , this coupling is about constant ( $113 \pm 2$  Hz) in the toluene, *m*-

xylylene and mesitylene derivatives II, VII, X, but it decreases as more  $\beta$ -substituents are introduced. This is borne out by a comparison of the ethyl and n-propyl derivatives III, VI, XI with the i-propyl and t-butyl compounds IV and V. Within the same series  $^3J(\text{Tl},p\text{-C})$  goes to more negative values from ethyl to t-butyl. Comparison of  $J(\text{Tl},m\text{-C})$  with  $J(\text{Tl},o\text{-C}_\alpha)$ , both being over the same number of bonds, shows the former (ca. 1050 Hz) to be roughly twice as large as the latter (ca. 450 Hz), as might be expected for a *cis-trans*-relationship. There are 3 different kinds of four-bond couplings, viz. one between Tl and  $o\text{-C}_\beta$ , one to  $m\text{-C}_\alpha$  and one to  $p\text{-C}$ . The larger size of the latter compared to the two first ones implies a substantial  $\pi$ -electron contribution.

The most interesting coupling is that over six bonds, i.e. from Tl to the  $p\text{-C}_\beta$  nuclei. In the ethyl and n-propyl compounds III and VI with a  $-\text{CH}_2\text{-C}$  sidechain,  $^6J$  is 48 and 47 Hz, respectively. In the i-propyl derivative ( $-\text{CH}-\text{C}_2$ ) one finds this  $^6J$  to be 29 and in the t-butyl one ( $-\text{C}-\text{C}_3$ ) 23 Hz. This behavior can be explained in conformational terms.  $\alpha$ -Substituted toluenes,  $\text{PhCH}_2\text{X}$ , are known [10] to favor a conformation in which the  $\text{C}_\alpha\text{-X}$  bond forms a right angle with the plane of the aromatic ring ( $\phi = 90^\circ$ ). The ground-state conformation of  $\alpha,\alpha$ -disubstituted toluenes,  $\text{PhCHX}_2$ , has been shown by NMR methods [11] to be such that the  $\alpha$ -protons lie in the plane of the aromatic system. Consequently the  $\text{C}_\alpha\text{-X}$  bonds form dihedral angles of  $60^\circ$  with that plane. t-Butyl aromatics can be assumed to have rather small sixfold rotational barriers whence  $\langle\phi\rangle = 45^\circ$ . The spin-spin coupling between an aromatic proton and  $p$ -methyl protons, which is transmitted exclusively through the  $\pi$ -system, shows a  $\sin^2$  dependence [12] on the dihedral angle between the  $\text{C}_\alpha\text{-H}$  bond and the benzene ring. This fact is due to the  $\sin^2\phi$  dependence of the  $\sigma\text{-}\pi$  interaction between benzylic protons and the adjacent carbon  $2p\pi$  orbital. If a similar mechanism dominates the present  $\text{Tl},p\text{-C}_\beta$  couplings, an analogous  $J(\phi)$  relation should exist. In fact, as the average dihedral angle decreases in the series  $\text{EtPhTlX}_2$  ( $\phi = 90^\circ$ ),  $i\text{-PrPhTlX}_2$  ( $\phi = 60^\circ$ ),  $t\text{-BuPhTlX}_2$  ( $\phi = 45^\circ$ ),  $^6J(\text{Tl},p\text{-C}_\beta)$  decreases from 48 to 29 to 23 Hz. An exact  $\sin^2\phi$  dependence is, however, not observed here, and a purely geometrical interpretation of the changes in coupling constants would certainly represent an oversimplification.

A 7-bond Tl,C-coupling in the n-propyl compound VI could not be detected. Comparison of the linewidth of the  $\alpha$ -carbon absorption to the width of the TMS signal allows  $^7J(\text{Tl},p\text{-C}_\gamma)$  to be estimated as  $< 1$  Hz.

The  $^1\text{H}$  spectra of the  $p\text{-Me}$ ,  $p\text{-Et}$  and  $p\text{-i-Pr}$ -phenylthallium trifluoroacetates II, III and IV show a decrease in  $^6J(\text{Tl},\text{H})$  from 64 to 46 to ca. 30 Hz, as  $\phi(\text{H}_\alpha\text{C}_\alpha\text{C}_m\text{C}_{ar})$  decreases from  $45^\circ$  to  $30^\circ$  to  $0^\circ$ . Hence the angular dependence of  $^6J(\text{Tl},\text{H})$  and  $^6J(\text{Tl},\text{C})$  is quite similar. A seven-bond Tl, H-coupling in the t-Bu-compound V could not be observed and must therefore be smaller than 1 Hz.

## Experimental

All arylthallium trifluoroacetates were synthesized by known procedures [13]. 12 mmol of the aromatic hydrocarbon were added to 25 ml (11.5 mmol) of a 0.46 molar solution of thallium tris(trifluoroacetate) in trifluoroacetic acid, and the mixture was stirred for 24 h at room temperature. When the reaction products precipitated, they were filtered off and dried, otherwise the solvent was evaporated after addition of 50 ml of 1,2-dichloroethane. Some products still contained

small amounts of residual starting material, but this did not interfere in the  $^{13}\text{C}$  NMR spectra.

NMR spectra were run in the PFT mode on a Varian XL-100-12 spectrometer at 25.16 MHz and 36°C. Except for the SFORD spectra, protons were noise-decoupled. The deuterium resonance of the solvent served for field-frequency stabilization. Spectral widths of 5 kHz and accumulation of 12K data points resulted in a resolution of 0.8 Hz/channel. Typically 10000 to 40000 pulses were accumulated and acquisition times of 1.2 sec/pulse.  $^1\text{H}$  NMR spectra were run on a Varian EM-360 spectrometer at 60 MHz and on the XL-100-12 spectrometer at 100 MHz.

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