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^{13}C NMR SPECTRA OF ARYLTHALLIUMTRIFLUOROACETATES: A CLARIFICATION

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Following our original report [1] of the chief features of the ^{13}C and ^{19}F NMR spectra of some arylthallium bis(trifluoroacetates) ($ArTl(OCOCF_3)_2$), Ernst [2] has discussed in detail the ^{13}C spectra of a more extensive selection of alkyl-substituted phenyl compounds. The reports of the ^{13}C spectra differ in the following respects:

(i) The one-bond couplings identified by us to be in the range 8841 Hz (for Ar = mesityl) to 9902 Hz (Ar = phenyl) [1] were not identified unequivocally in the second report [2].

(ii) The analysis of the (*ortho*, *meta*) carbon region of the spectra differed, leading to dissimilar values of $J(Tl—C_{meta})$ and $J(Tl—C_{ortho})$, and necessarily different $\delta(C_{meta})$ and $\delta(C_{ortho})$. Both analyses, however, yielded $J(Tl—C_{meta}) > J(Tl—C_{ortho})$. Our decisions were guided in part by data for other phenylmetal compounds.

(iii) The assignment strategy of Ernst [2] differed, and particularly in the case of Ar = *p*-tolyl, he reported observing, for two of the four lines (of the *ortho, meta* carbons) "almost resolved splittings at half height" due to the ^{203}Tl isotope γ ratio $^{205}Tl/^{203}Tl = 1.0097$) ($^{203}Tl$ 29.5%, ^{205}Tl 70.5%). This allowed pairing of the lines, and assuming least perturbation by the $Tl(OCOCF_3)_2$ group at *meta* positions, distinguished C_{ortho} and C_{meta}. This resolution of $^{203,205}Tl$ couplings, to be generally useful for assignment, would need to be observed readily in other suitable cases, e.g. Ar = phenyl, mesityl, but the situations here were not mentioned.

After accumulation of ca. 57 K pulses for both the Ar = *p*-tolyl and mesityl cases (THF solutions) we have not observed any resolution, nor preferential broadening of the signals of protonated aryl carbons, in good quality spectra. While Ernst [2] may have selected extremely favourable conditions in the Ar = *p*-tolyl case, our experience indicates that this criterion lacks generality. Nevertheless, we have conducted the essential clarifying experiment, which demon-

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strates quite clearly that Ernst's pairing [2] of the four (*ortho*, *meta*) signals in the *p*-tolyl case is correct, and presumably these values of $J(\mathrm{Tl{-}C}_{ortho})$ and $J(\mathrm{Tl{-}C}_{meta})$ are useful guides to couplings in other arylthallium systems.

m-Deuterotoluene (with ca. 80% D at one carbon) was synthesised (by standard manipulation of *m*-bromotoluene) and thallated by $\mathrm{Tl(OCOCF_3)_2}$ in $\mathrm{CF_3COOH}$ [3]. The product very rapidly crystallised from the solution and ^{1}H NMR analysis confirmed the structure and deuterium location. In the ^{13}C spectrum (THF-d_8 solution) of this deuterated compound the inner two of the four prominent aromatic-carbon lines are of appropriately reduced intensity and must be associated with carbon *ortho* to thallium.

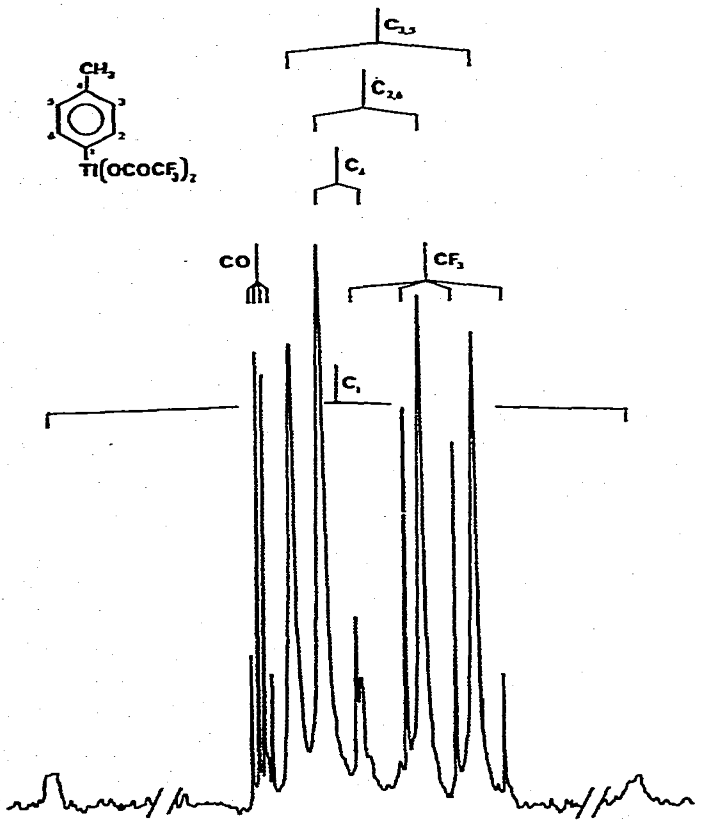

Fig. 1. The 22.63 MHz ^{13}C spectrum of *p*-tolylthallium bis(trifluoroacetate) (THF solvent). The resonances arising from the methyl-carbon and solvent are omitted. Assignments are as indicated and are discussed in the text.

In Fig. 1 is the spectrum (56 K pulses) of the *p*-tolyl compound, $\mathrm{(ArTl(OCOCF_3)_2)}$ and assignments are as indicated. The one-bond couplings, though weak and somewhat broad are quite clear and the J values were previously reported [1]. Also in Fig. 1 it is clear that resolution of ^{203,205}Tl coupling to the *meta*-carbon (i.e. C(3), C(5)) is imperceptible*. (This is also the case for our 57 K pulse spectrum of the mesityl compound, where the protonated aromatic carbon signals are relatively sharp.)

The J and δ values reported by Ernst [2] for the *ortho*, *meta* carbons, therefore should be adopted.

References

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*Our careful scrutiny of the published spectrum of the *p*-tolylthallium(III) compound [4] does not indicate any preferential broading or resolution of the *meta* carbon signals.