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SHORT COMMUNICATION

Coupling of the Methyl Carbon in the 13-C NMR Spectra of Some Fluoroaromatics, $C_6F_5XCH_3$

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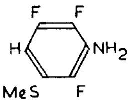
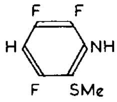
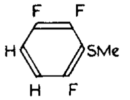
In the proton NMR spectra of methylamino, methoxy, and methythio fluoroaromatics, such as $MeSC_6F_5$, the methyl protons are split by coupling to the ortho fluorine atoms and the fluorine peaks in the corresponding fluorine NMR spectra are split into quarets by coupling to the three methyl protons [1]. This long range coupling has, in conjunction with other features of the proton and fluorine NMR spectra, allowed the structures of various fluoroaromatics such as $(MeS)_xC_6F_yX_z$ (X = F, H, Cl etc.) to be deduced [2-7]. In the amino derivative $NH_2C_6HF_3(SMe)$, prepared from 1,2,4,5-tetrafluoroaniline [8], the ^{13}C spectrum was examined to determine whether the structure was I or II.


(I)


(II)

In this spectrum the methyl carbon was split into a doublet, J=2.25 Hz. The origin of this could be coupling to the ortho fluorine through a system C-S-C-C-F. The magnitude of the coupling is similar to that observed for coupling in a C-C-C-C-F system [9].

The methyl ^{13}C NMR spectra of a number of analogous compounds, C_6F_5SMe, p-$(MeS)_2C_6F_4$, p-$F_2C(SMe)_4$, $C_6(SMe)_6$, III, IV, and V were examined.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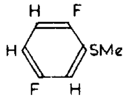
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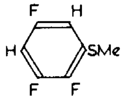
(V)

In $C_6(SMe)_6$ the methyl proton was observed as a single sharp peak. The methyl carbon was split into a doublet in I, IV, and V and into a triplet in C_6F_5SMe, p-$(MeS)_2C_6F_4$, p-$F_2C_6(SMe)_4$, and III. Details of the spectra are tabulated in Table I.

TABLE I

Methyl Carbon ^{13}C NMR Spectral Data

Compound	Chemical Shift (p.p.m.)	Coupling Constant (H7)
$C_6(SMe)_6$	21.114 S	---
C_6F_5SMe	18.148 T	3.14
p-$(MeS)_2C_6F_4$	17.695 T	1.76
p-$F_2C_6(SMe)_4$	18.662 T	3.86
I	16.055 D	2.25
III	17.659 T	3.80
IV	14.585 D	2.03
V	15.053 D	2.45
C_6F_5OMe	62.897 T	3.41
C_6F_5NMeH	33.588 T	4.40
$C_6F_5NMe_2$	43.602 T	3.45
C_6F_5COMe	32.592 T	2.42

S = Singlet, D = Doublet, T = Triplet

From the spectrum of $C_6(SMe)_6$ it is clear that the origin of the coupling involves either proton or fluorine and from the compounds C_6F_5SMe, *p*-$(MeS)_2C_6F_4$, and *p*-$F_2C_6(SMe)_4$ that the coupling is to fluorine rather than to hydrogen. Comparison of the structures of III, IV, and V show that the coupling is to *ortho* fluorine rather than *meta* or *para* fluorine. If the coupling were to *meta* fluorine the methyl carbon spectrum of I, III, and IV would be a doublet, and of V a triplet. If the coupling were to a *para* fluorine the methyl carbon peak would be observed as a singlet in (*p*-MeS)$_2C_6F_4$, *p*-$F_2C_6(SMe)_4$, III, IV, and V or a doublet in C_6F_5SMe and I. The compound *p*-$F_2C_6(SMe)_4$ has a symmetrical structure and the methyl protons in the ^{1}H NMR spectrum should be expected to appear as doublets, however triplets are observed [3]. The splitting of the methyl carbon into a triplet in the ^{13}C NMR spectrum also cannot be explained on the basis of a first order spectrum.

The methyl carbon spectra of other fluoroaromatic systems C_6F_5XMe (X = O, NH, NMe, CO) have been examined. In all cases the methyl carbon was split into a triplet by coupling to the *ortho* fluorine atoms. The splitting is therefore observed through a system F-C-C-X-C, where X = O, N, C or S. The ^{13}C NMR spectra of the methyl carbon in substituted fluoroaromatics can be used to determine the structure of the fluoroaromatics or as a further confirmation of the structures derived from other spectra.

EXPERIMENTAL

The reagents were available commercially or prepared by standard literature methods: C_6F_5SMe [2], *p*-$(MeS)_2C_6F_4$ [2], *p*-$F_2C_6(SMe)_4$ [2], $C_6(SMe)_6$ [10], I [8], III [4], IV [4], V [4], C_6F_5NHMe [11], $C_6F_5NMe_2$ [12].

The NMR spectra were recorded in $CDCl_3$ solution on a Varian XL-100 with the proton decoupled using TMS as internal standard.

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