

Long-range ^{19}F -H Coupling and Hindered Rotation

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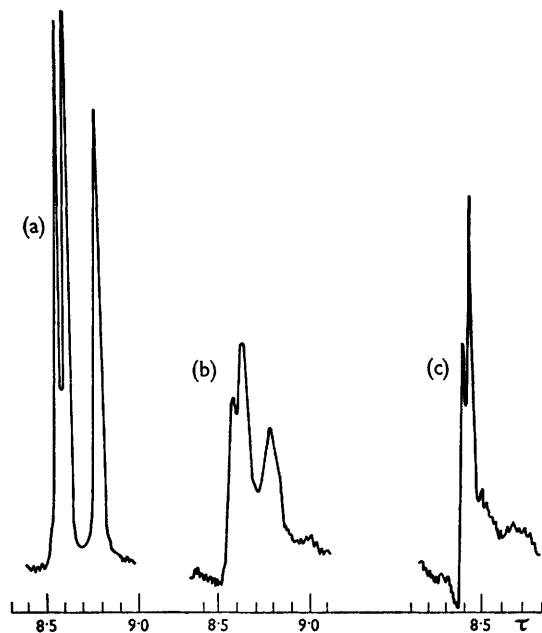
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LONG-RANGE COUPLING has been reviewed, and discussed in terms of specific arrangements of the nuclei involved.¹ Particular emphasis has been placed on the requirement of a near planar zig-zag configuration.^{2,3} Long-range coupling between

nuclear and side-chain protons is not normally observed in the nuclear magnetic resonance spectra of aromatic compounds. However, ^{19}F -H coupling has been detected between ring fluorine atoms and side-chain protons separated by five

bonds.^{4,5} It was suggested that these couplings are "through space" and not through the five bonds although an angular dependence might be involved as well as a proximity factor.

(through five bonds) or to methyl substituents (through six bonds). In the proton magnetic resonance spectrum of (Ie), determined at 33°, the absorption due to the *t*-butyl group shows as a doublet (six protons) at τ 8.6 [$J(F'-H)$ 2.9 c./sec.] and a singlet (three protons) at τ 8.8 [Figure (a)].



FIGURE

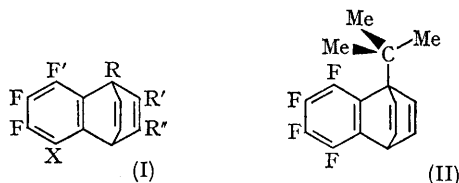
We have previously reported the isolation of a 1,4-adduct formed by the reaction of tetrafluorobenzene with benzene.⁵ In our further studies on the orientation of the 1,4-addition of tetrafluorobenzene to substituted benzenes we have observed pronounced long-range coupling between aromatic ring fluorine atoms and protons separated by as many as six bonds. These results are most easily explained in terms of a "through space" coupling to $F'(I)$ involving angular dependence as well as a proximity factor (Table).

Compounds of the type (If) show no detectable $^{19}F-H$ long-range coupling to the vinyl protons

Compound (I)	$J(F'-H^R)$ at 33°
(Ia) $R=R'=R''=-H$; $X=Br$	≈ 1.9 c./sec.*
(Ib) $R=Me$, $R'=R''=H$; $X=F$	≈ 5.1
(Ic) $R=OMe$, $R'=R''=H$; $X=F$	≈ 2.6
(Id) $R=NMe_2$, $R'=R''=H$; $X=F$	≈ 3.8
(Ie) $R=Bu^t$, $R'=R''=H$; $X=F$	≈ 2.9
(If) $R=H$, $R'=R''=Me$; $X=F$	$\approx 0^\dagger$

* determined from the ^{19}F n.m.r. spectrum
 $\dagger J(F'-H^R)$

On heating the sample the spectrum remains virtually unchanged until 120° when the signal begins to collapse [Figure (b)]. At 180° the signal begins to resolve into a doublet [at τ 8.42; $J(F'-H) \approx 2.1$ c./sec.] and at the maximum temperature studied (200°) the coupling constant is 2.2 c./sec. [Figure (c)]. The original spectrum is observed on cooling the sample to room temperature.



We suggest that these results prove that rotation of the tertiary butyl group is severely hindered and that the orientation at room temperature is as shown (II).

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¹ S. Sternhell, *Rev. Pure Appl. Chem. (Australia)*, 1964, **14**, 15.

² M. Martin-Smith, S. T. Reid, and S. Sternhell, *Tetrahedron Letters*, 1965, 2393.

³ K. C. Ramey and J. Messick, *Tetrahedron Letters*, 1965, 4423.

⁴ J. Burdon, *Tetrahedron*, 1965, **21**, 1101.

⁵ P. C. Myhre, J. W. Edmonds, and D. J. Kruger, *J. Amer. Chem. Soc.*, 1966, **88**, 2459.

⁶ J. P. N. Brewer and H. Heaney, *Tetrahedron Letters*, 1965, 4709.