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NMR AND ESR INVESTIGATIONS OF FLUORINATED PHENYL-t-BUTYL NITROXIDE RADICALS. MECHANISMS OF SPIN TRANSMISSION

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The NMR and ESR measurements on proton hyperfine splitting constants in aromatic t-butyl nitroxides are in good agreement with each other,[1] and these studies have now been extended to nitroxides containing fluorine. Since the NMR method also gives the absolute sign of the splitting constant, we have here the possibility to investigate fluorine hyperconjugation and spin transmission mechanisms.

The experimental data are collected in Table I. Despite the widely different experimental conditions of the two methods, the agreement is good. The differences are mostly due to the lower accuracy of the ESR method in this system and to the concentration dependence of the ^{19}F NMR shift. The splitting constants are calculated from the NMR contact shifts by using the following equations:

$$a_H = -1.37 \times 10^{-2} \times \Delta\sigma \quad (304^\circ K)$$

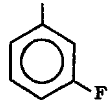
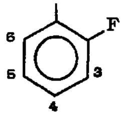
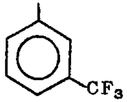
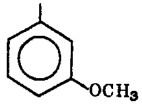
$$a_F = -1.29 \times 10^{-2} \times \Delta\sigma$$

a_H and a_F are the proton and fluorine hyperfine splitting constants (gauss) and $\Delta\sigma$ is the shift in ppm. (positive in the upfield direction) for the nucleus with reference to its position in a related diamagnetic compound (the hydroxylamine).

Alternating spin density in the carbon skeleton is a general feature for this class of radicals whether they are sterically hindered or not.[1, 2] The spin is transmitted to the ring protons via a spin polarisation mechanism, which predicts inversion of the absolute sign in comparison to that of the attached carbon atom. However, the situation is changed when free electron lone pairs are available on the spin nucleus attached to the aromatic ring. If a resonance structure such as Ib represents the dominating mechanism for transmitting the

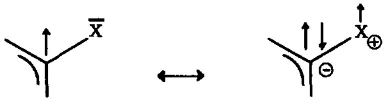
TABLE I

Hyperfine Splitting Constants Obtained for $\mathrm{ArN\dot{O}}$-*t*-Bu by ESR and NMR Spectroscopy (304°K, in $CDCl_3$)

Compound	Mp. °C hydroxyl-amine	Spectro-scopic method	a_N	a_2	a_3	a_4	a_5	a_6	$a_{t\text{-Bu}}$	a_F	Ref.
	112	ESR*	12.65	1.95	-	1.95	0.95	1.95	-	0.95	6
		NMR		-2.03	-	-2.03	+0.91	-2.03	-0.056	-0.94	
	128-131	ESR**	14.2	-	0.58	0.56	0.90	1.04	0.25	1.35	1b
		NMR		-	+0.59	-0.56	+0.89	-1.03	-0.23	+1.37	
	102-103	ESR*	12.5	2.0	-	2.0	0.7	2.0	-	0.7	6
		NMR		-1.92	-	-1.92	+0.85	-1.92	-0.062	-0.62	
	89-90	ESR*	12.8	1.94	-	1.94	0.78	1.94	-	-	6
		NMR		-1.86	-	-1.86	+0.79	-1.86	-0.082	-0.017***	

*in diethylene glycol, room temperature; **in methylene chloride, -50°C; ***OCH_3

unpaired spin, then the spin leaks out on the substituent with conservation of its sign. Our results show that irrespective of the location of the substituent



Ia ⟷ Ib

$X = F, OR, NR_2, SR, PR_2$

on the aromatic ring, the sign of the splitting constant for ring fluorine is opposite to that of the ring proton (Table I, Fig.1). This effect has been noted earlier from the ^{19}F NMR contact shifts in some transition metal aminotroponiminates.[3]

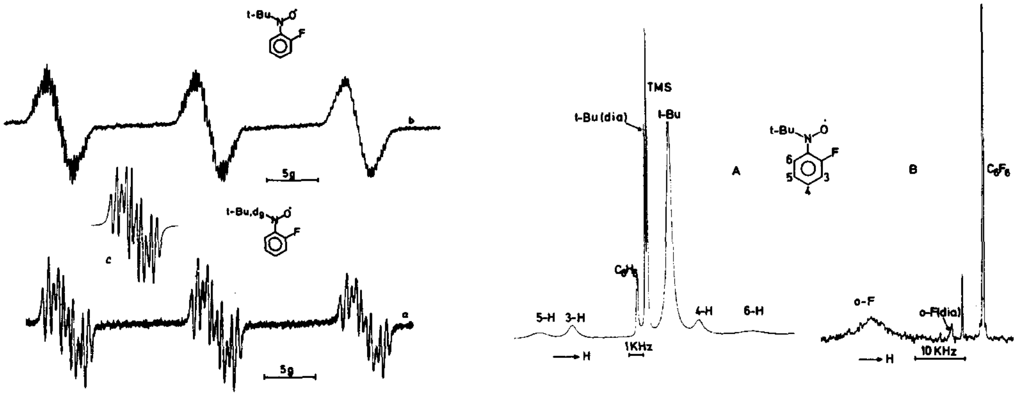
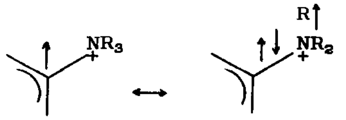
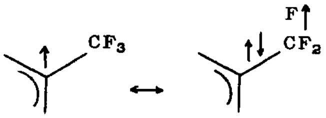


Fig.1. ESR (a: t-Bu,d_9 ; b: t-Bu,H_9 ; c: simulated) and NMR spectra (A: H-region; B: F-region) of o-fluoro-phenyl-t-butyl nitroxide

Preliminary results show that the resonance effect dominates when free pairs of electrons are available on the substituent, i.e., when X equals F, OR[1a], NR_2, and presumably PR_2 and SR. The sign of the R coupling is therefore expected to be changed by quaternization of the amino group. This is now explained by the hyperconjugative mechanism II.



II



III

By substitution on S or P one should be able to arrive at a measure of the $p\pi$-$d\pi$ overlap. Works in this direction are in progress.

It was of interest to determine the absolute sign of the CF_3 coupling, because this would solve some of the controversy about fluorine hyperconjugation.[4] With the CF_3 group in meta position - negative spin density on carbon - a hyperconjugation mechanism predicts a negative spin on fluorine, III, and this was actually found, Table I. The ortho-trifluoromethyl phenyl-t-butyl nitroxide gave a positive splitting constant, +0.83 gauss, for the CF_3 group, i.e., it behaves similarly to the CH_3 group.[2] It may be noted that the signs of the hyperfine splitting constants are in agreement with the signs of the π-electron contributions to CH_3-^1H, CH_3-^{19}F, and CF_3-^1H NMR long-range coupling constants.[5]

Methoxy protons in ortho- and para-position have positive splitting constants,[1a] whereas those in the meta position have negative splitting constants, which is explained by the dominating resonance effect Ib and hyperconjugation. Dialkylamino protons behave in the same way.

The compounds were prepared according to standard methods, and gave satisfactory analytical and spectroscopic data. The ESR spectra were obtained by direct generation of the aryl-t-butyl nitroxides in the cavity of a Varian E3 instrument. The appropriate iodides were photolyzed in methylene chloride solution in the presence of t-nitrosobutane or t-nitrosobutane,d_9 as scavenger.[7]

The NMR spectra were recorded on a Varian XL-100-15 spectrometer (40.96 KHz modulation) by sweeping the V3508 flux stabilizer. The smallest possible sweep width (25 Hz) was chosen on the recorder so that the change of 0.5 Hz/cm in frequency could be completely neglected. Sweep calibration were obtained from samples containing reference peaks, for which the frequency separation was determined in the usual internal lock mode. The sample temperature was 304°K.

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