

R. W. Kreilick,
J. Chem. Phys., **45**, 1922 (1966).

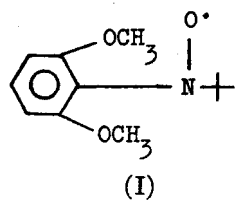


FIG. 1. One hundred-megahertz NMR spectrum of Radical I in CH_2Cl_2 .

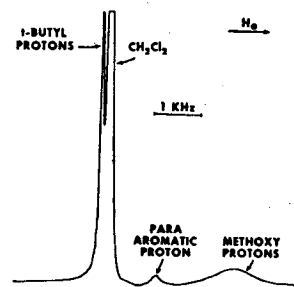


TABLE I. One hundred-megahertz NMR shifts of Radical I.

Proton	Shift ^a (Hz)	Linewidth (Hz)	Hydroxylamine chemical shifts ^b	Calculated a_i (Oe)
OCH_3	+2690	830	378	-0.33
<i>p</i> -Aromatic	+1020	240	700 ^c	-0.16
<i>t</i> -Butyl	-420	90	110	+0.08

^a From internal CH_2Cl_2 .
^b From TMS.

^c This value is estimated, as the NMR spectrum is a series of broad lines.

J. Goldman et al., *Tetrahedron*, **29**, 3843 (1973).

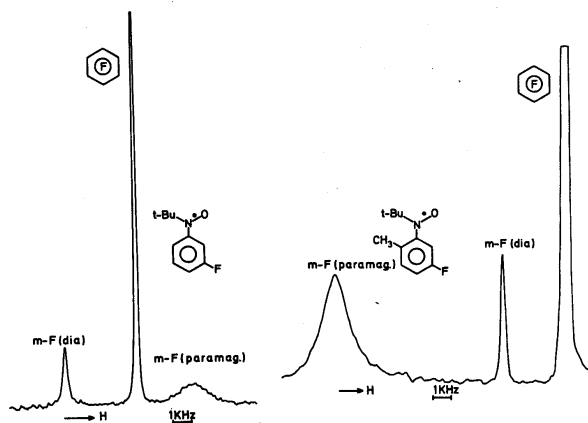


Fig 4. ^{19}F NMR spectra of *t*-butyl-3-F-phenyl nitroxide and *t*-butyl-5-F-2-Me-phenyl nitroxide. The figure shows the effect of *ortho*-substitution on the direction of the F-shifts.

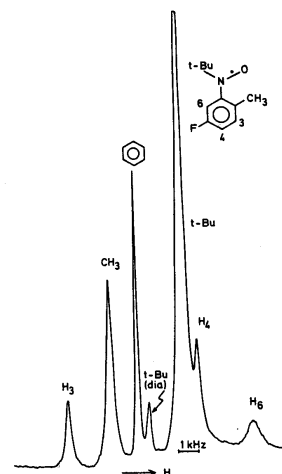


Fig 5. ^1H NMR spectrum of *t*-butyl-5-F-2-Me-phenyl nitroxide.

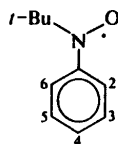


Table 1. Hyperfine splitting constants (gauss) obtained for ArNO-t-Bu by ESR and NMR spectroscopy

Compound	Spectroscopic method	a_N	a_2	a_3	a_4	a_5	a_6	a_{t-Bu}
1 2-6 = H	ESR ^a	13.0	1.9	0.8	1.9	0.8	1.9	
	NMR		-1.82	+0.87	-1.82	+0.87	-1.82	-0.093

A. R. Forrester and S. P. Hepburn, *J.C.S. Perkin I*, **1974**, 2208.

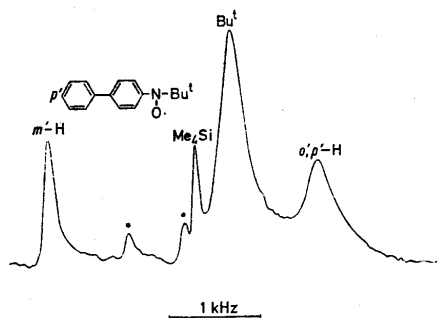


FIGURE 2 N.M.R. spectra of biphenyl-4-yl *t*-butyl nitroxide (asterisks denote peaks due to diamagnetic impurity)

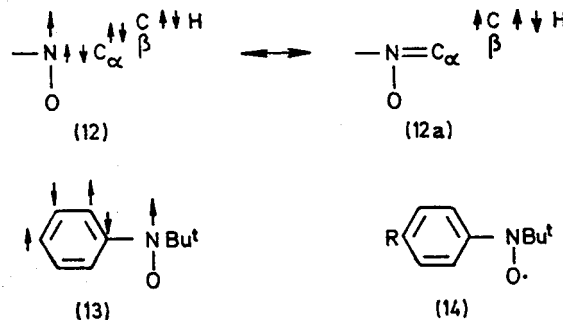
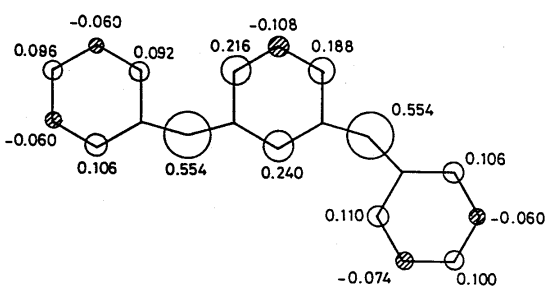


Table 1. ENDOR Spectra and Hfs Constants of Aminoxyl Radicals

Radical	Structure	ENDOR spectra (in toluene, -70 °C)	ENDOR	Hfsc/10 ⁻⁴ T ⁵⁻⁷ NMR
2,2,6,6-Tetramethyl- piperidine-1-oxyl-4-ol (TEMPOl)			0.48 (CH ₂) 0.40 (CH ₃) 0.25 (CH ₂)	-0.48 (βCH ₂) -0.45 (αCH ₃) -0.31 (βCH ₂) +0.07 (γCH) -0.02 (αCH ₃)
2,2,6,6-Tetramethyl- piperidine-1-oxyl-4-one (TEMPONE)			0.13	-0.12 (αCH ₃) -0.02 (βCH ₂)
2,2,6,6-Tetramethyl- piperidine-1-oxyl (TEMPO)			0.37 (CH ₂) 0.18 (CH ₃)	-0.39 (βCH ₂) -0.23 (αCH ₃) +0.18 (γCH ₂)
2,2,5,5-Tetramethyl- pyrrolidine-1-oxyl- 3-carboxamide			0.32	
Di-t-butylaminoxyl (DTBN)			0.10	0.10

a) ENDOR

T. Takui et al.,
Mol. Cryst. Liq. Cryst.,
176, 67 (1989).



Ph-C: -C₆H₄-C: -Ph

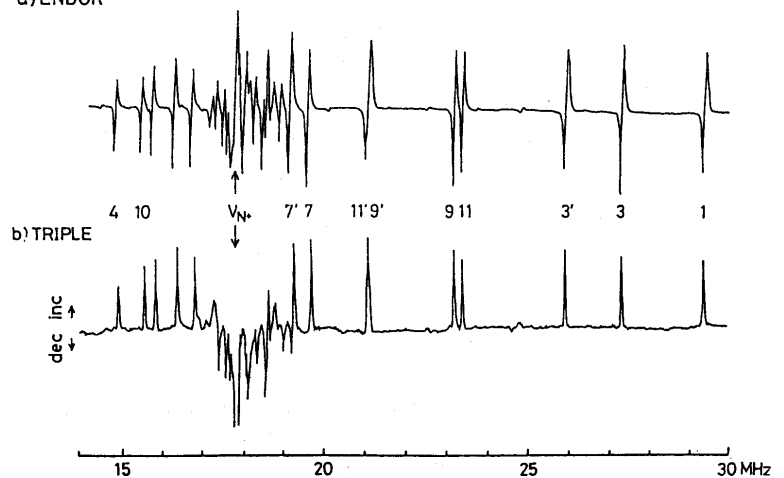


FIGURE 2. ¹H-ENDOR (a) and TRIPLE (b) spectra of m-PBPM observed at 4.2K when the ESR line B₊ was monitored with the external magnetic field parallel to the b axis of the benzophenone-d₁₀ host crystal. The free proton NMR frequency ν_{N+} was 17.7607 MHz.

スピン分極

ESR ではスピン密度 の絶対値しかわからないので、NMR や ENDOR/TRIPLE で符号を決定する。

NMRで、 $\Delta H = -a_N \frac{\gamma_e}{\gamma_N} \frac{g\beta H}{4kT}$, ESRで、 $a_N = \rho_{NP}$ (McConnell 式), 要するに、 $\rho \propto a_N \propto \Delta H$ 。

なお、固体では、中性子線回折という方法もある。