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PROTON AND NITROGEN-14 ENDOR SPECTRA OF AMINOXYL SPIN ADDUCTS FROM PBN

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Both N-14 and proton hyperfine splittings have been observed in the ENDOR spectra of spin adducts of phenyl t-butyl nitrone (PBN). From the differences in relative intensities of the ENDOR doublets the relative signs of the coupling constants can be ascertained.

Proton[1-10] and N-14[11-17] ENDOR spectra of aminoxyl radicals (nitroxides) have appeared in the literature. However few instances where both the proton and N-14 ENDOR lines are detectable at the same temperature are available.[14,17] This communication describes some ENDOR results obtained from an investigation of the relative intensities of the proton and N-14 lines of spin adducts of PBN recorded at the same temperature. Figure 1 shows the ENDOR spectra of three spin adducts of PBN (t-butoxyl, I; benzoyloxyl, II; phenyl, III) in benzene at 279, 285, and 290 K respectively. The N-14 doublet is strong at these temperatures and the β- and γ-H doublets are also visible. The obtained hyperfine splitting constants (hfsc's) are compared to those reported by Kotake and Kuwata[6] in Table 1. The β-H hfsc's reported here are 0.4-0.5 MHz larger while the γ-H hfsc's are smaller by 0.1-0.2 MHz. The differences in the β-H hfsc's could be due to the difference in temperature used for the ENDOR determinations. Thus for the phenyl adduct, III, a_N = 14.37 and a_β^H = 2.16 G at 290 K in toluene.[18] The ENDOR N-hfsc is probably less accurate because it depends on the absolute frequency calibration of the RF oscillator.

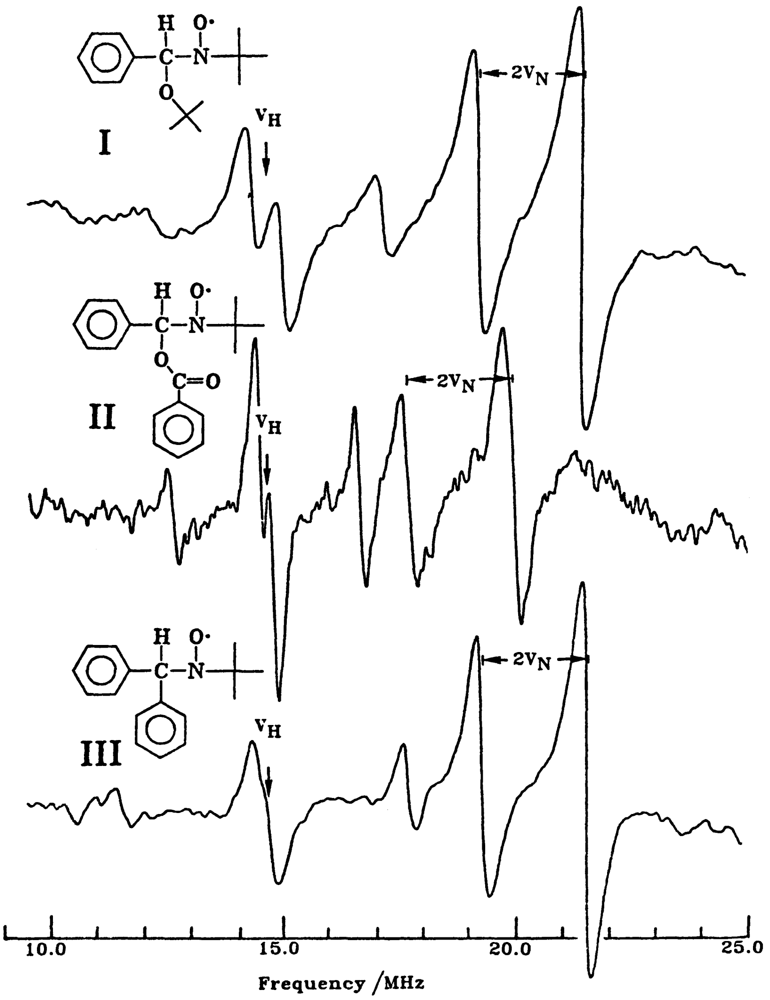

Fig. 1.

Table 1. Hyperfine Splitting Constants of PBN Spin Adducts[a) c)]

Structure of R	Figure	N-14	β-H	γ-H
Me_3CO	I	(+)40.55 (14.48)	(+)4.84 (1.73)	(-)0.70 (0.25)
PhCOO	II	37.01 (13.22)	3.96 (1.41)	0.30 (0.11)
			3.42 (1.22)b)	0.40 (0.14)b)
Ph	III	(+)40.80 (14.57)	(+)6.05 (2.16)	(+)0.26 (0.09)
			(+)5.67 (2.03)b)	(+)0.47 (0.17)b)

a) In benzene in MHz (Gauss). b) In toluene at 240 to 180 K, Ref. 6.
c) Signs determined by CRISP based on $a_N>0$.

The relative intensity patterns of the ENDOR doublets depend on which component of the N-14 triplet is saturated. Figure 2 shows the spectra

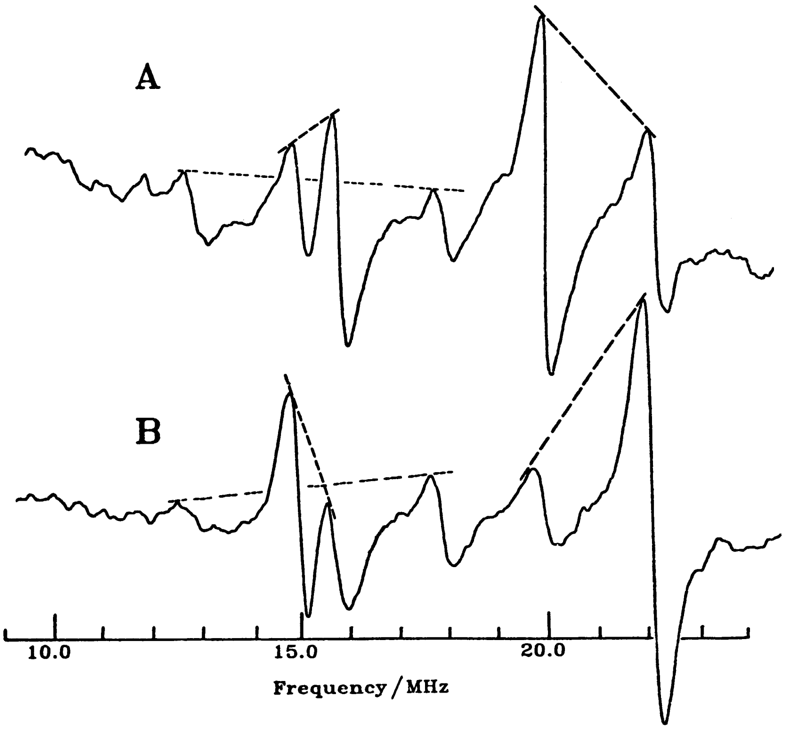

Fig. 2.

obtained when the M_I = +1 or M_I = -1 component of the N-14 triplet from I is saturated. If the intensities of the lines are labelled "w" or "s" (for weaker or stronger) it is evident that the intensity sequence is the same for the β-H and the N-14 doublet but reversed for the γ-hydrogen and the N-14 doublet.

Table 2. Relative Intensities of ENDOR Doublets

Figure	N-14 line saturated	N-14	β-H	γ-H
2B	M_I = +1	w,s	w,s	s,w
1	M_I = 0		reference	
2A	M_I = -1	s,w	s,w	w,s

This effect[19,20)] follows the relative intensity sequence patterns found for the N-14 ENDOR doublets themselves[11,13-16)] if the sign of the coupling constant is the same (and the opposite if the sign is opposite). Since such intensity differences are useful for ascertaining the relative signs of hyperfine splitting constants for free radicals, we propose the name Cross Relaxation Intensity Sequence Pattern (CRISP) for this method.

PBN was 0.1 M; 10-20 mg of initiator was used (di-t-butylperoxalate for I, benzoyl peroxide for II and phenylazotriphenylmethane for III). The solvent was nitrogen degassed[21)] and a small flat cell was used.[22)] An IBM ER-200D-SRC EPR

ENDOR/TRIPLE spectrometer with a 300W RF amplifier was used for this work. All experiments were done at IBM Instruments Inc. San Jose, California. The authors are grateful for support of this work and continuing assistance from the Natural Sciences and Engineering Research Council of Canada. Inspiration for the use of ENDOR for spin trapping work dates to 1972 when one of us (EGJ) was influenced by association with Dr. Y. Kotake in Prof. K. Kuwata's laboratory.

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