CHEMISTRY LETTERS, pp. 111 - 114, 1985.

^{1}H-ENDOR OF DI-t-BUTYL NITROXIDE
EFFECT OF THE ^{14}N HYPERFINE INTERACTION

Jun YAMAUCHI* and Yasuo DEGUCHI
College of Liberal Arts and Sciences, Kyoto University, Kyoto 606

ENDOR spectra of di-t-butyl nitroxide have been observed at -90 °C in heptane. Two ENDOR lines near the free proton frequency had different absorption intensities and their line-shape showed a clear dependence on the nitrogen spin quantum number. This indicates an important spin cross relaxation by the nitrogen nucleus in the proton spin system and suggests a negative sign of the proton hyperfine coupling constant.

The electron nuclear double resonance (ENDOR) of a ^{14}N nucleus in di-t-butyl nitroxide (DTBNO) has been reported in this letter communication.1) Two ENDOR lines due to the ^{14}N nucleus showed non-equivalent intensities and a clear dependence on the nitrogen nuclear spin quantum number of the observing ESR line. These phenomena were first observed in some nitroxide radicals similar to DTBNO by Leniart et al.,2) and were attributed to a cross relaxation due to an anisotropic hyperfine coupling between the electron and ^{14}N nuclear spins.

Additionally the letter communication commented an unsuccessful observation of appreciable ^{1}H-ENDOR signals of DTBNO. However, a more deliberate choice of a proper radical concentration enabled us to observe the ^{1}H-ENDOR of DTBNO, which indicates also a line-shape dependence on the ^{14}N nuclear spin quantum number. ^{1}H-ENDOR signals have been reported in some aminoxyl radicals frequently used in spin-probe-spin-label method, including DTBNO, by Kotake and Kuwata.3) In this communication we would like to point out that this ^{1}H-ENDOR line-shape implies an influence of the ^{14}N hyperfine interaction to the spin relaxation in the proton spin system, which may be called a secondary effect of ENDOR spin relaxation.

Samples were prepared by dissolving liquid DTBNO (Eastman Kodak Co,, reagent grade) in heptane and then degassing this solution by usual freeze-pump-thaw technique. A radical concentration could not be changed because of a volatile nature of DTBNO. Therefore, for a proper choice of the radical concentration we had to prepare a lot of samples with a different radical concentration. A considerably dilute limit (ca. $2X10^{-5}$ mol dm^{-3}) was found to be suitable for a good ^{1}H-ENDOR observation. ENDOR experiments were carried out by using a TM mode cavity and experimental arrangements were same as reported in the literature.[1,4)]

An ESR spectrum of DTBNO shows three main lines due to the nitrogen hyperfine interaction as is shown in Fig. 1. There are two main nuclear spins in DTBNO. However, the nitrogen nucleus has a far bigger coupling constant than the t-butyl protons and the ^{1}H hyperfine coupling is so small to be resolved. This fact implies a far bigger anisotropic hyperfine interaction between the electron and ^{14}N nuclear spins and a negligibly small anisotropic hyperfine interactions between the electron and ^{1}H nuclear spins. Therefore, a spin cross relaxation in the proton through the anisotropic proton hyperfine interaction is expected to be quite small. Thus, the spin relaxation in the proton system, if any, would take place through the nitrogen energy levels by the nitrogen anisotropic hyperfine interaction. This is the case as is observed in the ^{1}H-ENDOR shown in Fig. 2, where the observing ESR line in the ENDOR experiment is designated by the nitrogen nuclear spin quantum number, m_I=1, 0, -1 in Fig. 1.

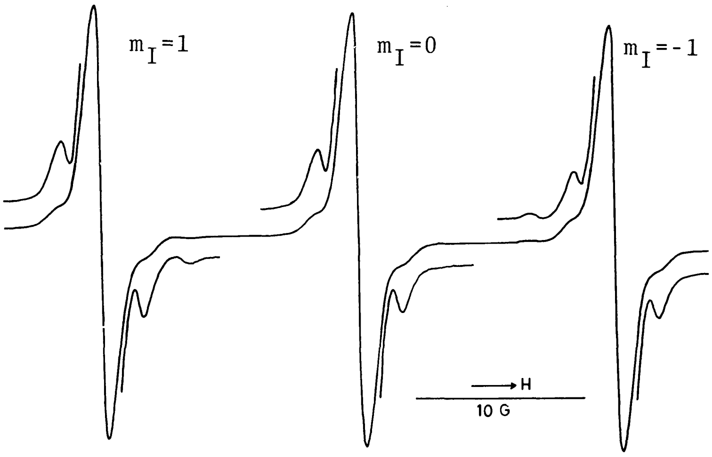

Fig. 1. ESR spectrum of DTBNO.

The central ^{1}H-ENDOR absorption seems to be one line, but it splits into two lines, although imperfectly, when a FM modulation in the ENDOR observation is lowered. By a spectrum analysis of this central ^{1}H-ENDOR, t-butyl hyperfine coupling constant 0.14_0 G† was obtained, in quite good agreement with the value determined from an NMR Knight shift measurement (0.15 G in the dilute limit).[5)]

---

† 1 G = 10^{-4} T.

The upper and lower ^{1}H-ENDOR spectra show inequivalent absorption intensities. For instance, when the higher field ESR line is observed (m_I=-1), then the high frequency ^{1}H-ENDOR intensity is bigger than the low frequency one. On the other hand, the ^{14}N-ENDOR pattern in the same conditions shows a bigger low frequency line and a weaker high frequency line.1) This relation between the ^{1}H- and ^{14}N-ENDOR patterns is reversed in the ENDOR observation monitoring the low field ESR (m_I=1). Thus, the proton spin relaxation is more greatly influenced by the nitrogen cross relaxation than by the proton spin relaxation itself. This is because of the far larger nitrogen and almost negligible proton hyperfine coupling constants.

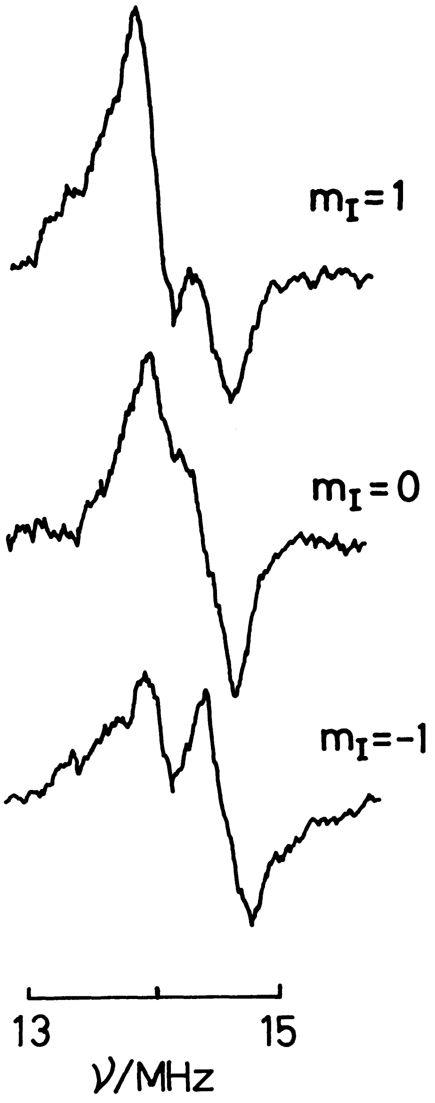

Fig. 2. ^{1}H-ENDOR signals of DTBNO observed with the magnetic field on each of the ESR lines.

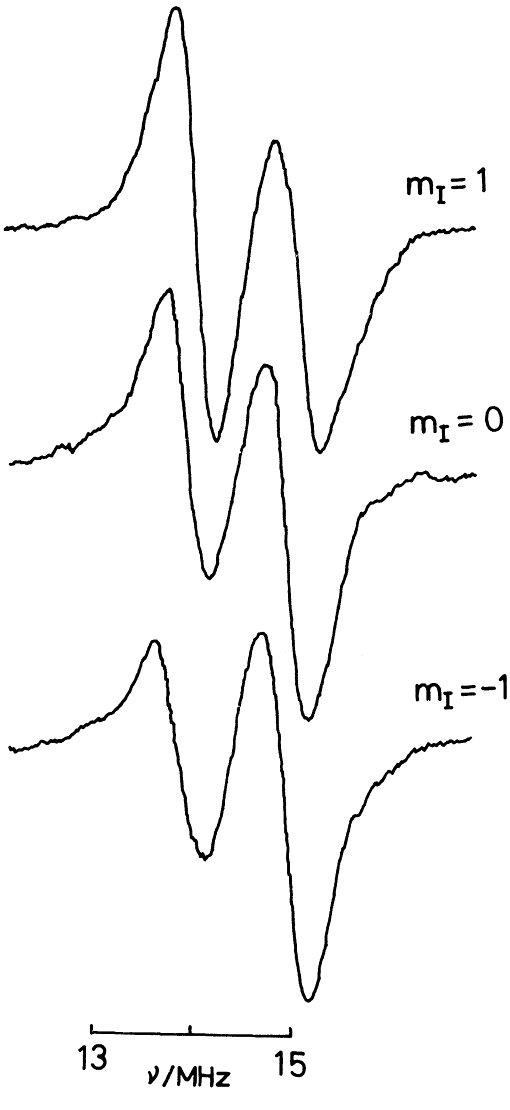

Fig. 3. ^{1}H-ENDOR signals of TANOL observed with the magnetic field on each of the ESR lines.

The intensity ratios between the high and low frequency lines in the ^{1}H- and ^{14}N-ENDOR spectra are opposite. This means opposite signs of the proton and nitrogen hyperfine coupling constants. If one assumes a positive sign in the ^{14}N hyperfine coupling constant as is expected for usual nitroxide radicals, this experiment results in a negative sign in the proton hyperfine coupling constant. This also agrees well with the data determined from the Knight shift measurement.[5)]

Finally it should be noted that the similar effect to this experiment was observed in another nitroxide radical, 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl (usually called TANOL). Proton coupling constant in this radical is slightly larger than that in DTBNO, so that unequivalent doublet lines in the ^{1}H-ENDOR are clearer as is shown in Fig. 3.

Recently proton and nitrogen-14 ENDOR spectra of aminoxyl spin adduct were reported by Janzen and Oehler, who observed the differences in relative intensities of the ENDOR doublets in their radicals. This would be the same phenomena in two-spin ENDOR system.[6)] They proposed the name Cross Relaxation Intensity Sequence Pattern (CRISP) for the method of ascertaining the relative signs of hyperfine coupling constants from the intensity differences in the ENDOR pattern.

More detailed report will be published in due course together with a quantitative analysis in DTBNO and other nitroxide radicals.

References

1) J.Yamauchi and Y.Deguchi, Chem.Lett., 1983, 257.
2) D.S.Leniart, J.C.Vedrine, and J.S.Hyde, Chem.Phys.Lett., 6, 637 (1970).
3) Y.Kotake and K.Kuwata, Chem.Lett., 1984, 83.
4) J.Lopez, J.Yamauchi, K.Okada, and Y.Deguchi, Bull.Chem.Soc.Jpn., 57, 673 (1984).
5) R.W.Kreilik, J.Chem.Phys., 45, 1922 (1966).
6) E.G.Janzen and U.M.Oehler, Chem.Lett., 1984, 1233.
Our experiment which concerns with the same phenomena was carried out independently and a part of the result was presented in the annual ESR symposium of the Chemical Society of Japan (1983). Their paper prompted us to make a short communication.

(Received October 18, 1984)