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^{14}N ENDOR OF DI-t-BUTYL NITROXIDE

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ENDOR spectra of di-t-butyl nitroxide have been observed at -104°C in heptane and two ENDOR lines only due to ^{14}N nucleus have been detected. The observed intensity indicates that cross relaxation is an important means of spin relaxation as has been revealed in some alicyclic nitroxide radicals.

The electron nuclear double resonance (ENDOR) technique has been applied to a number of organic free radicals in solution and its theory was developed by Freed[1)] more than ten years ago. Now it is well established that the ENDOR response of a radical in solution depends considerably on the spin relaxation process. However, there are only a few examples of ENDOR in the liquid phase from nuclei other than protons. This is partly because most of the nuclear gyromagnetic ratios are much smaller than that for protons. In the case of the radicals which have large isotropic hyperfine coupling constants the ENDOR absorption lines are expected to be observable.

The observation of ^{14}N ENDOR of a radical in solution was first reported by Leniart et al.[2)] for some alicyclic nitroxide radicals. The ^{14}N nucleus has a small quadrupole moment, which can contribute to the short nuclear relaxation in solution. This quadrupole splitting was also determined from the nitrogen ENDOR spectra of alicyclic nitroxide radicals in liquid crystals.[3)] Atherton and Brustolon[4)] observed very weak solution ENDOR spectra due to ^{14}N nucleus of peroxylamine disulfonate ion, $(SO_3)_2NO^{2-}$, radical in aqueous solution. In addition to these examples there are only few reports of ^{14}N ENDOR.[5,6)] Special experimental conditions seem to be required for the observation of ^{14}N ENDOR because of the special nuclear relaxation behavior, so that the radical species are quite limited so far.

In this letter we would like to report the ^{14}N ENDOR observation of di-t-butyl nitroxide (DTBNO). In this molecule an alicyclic bridge as in alicyclic nitroxide radicals is removed so that the more degrees of freedom of molecular motions may be expected. This trend would be enhanced by its sphere-like molecular structure, leading to the more complicated and rapid relaxation behavior. This is probably one of the reasons why the ^{14}N ENDOR of DTBNO is not reported so far.

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. Once the sample tube was sealed off under high vacuum, a radical concentration of DTBNO could not be changed because of a volatile nature of the radical. The ENDOR measurements were carried out with a high rf power (ENI-type A300 power amplifier), continuous wave-type spectrometer (JEOL ES-EDX2, FE-3X spectrometer) operating at X-band microwave frequency and with an 80 Hz field modulation. The sample cavity is a modified version of the TM mode cavity developed by Mobius and Biehl.$^{7)}$ The experimental details will be described elsewhere.

Figure 1 shows an ESR spectrum of DTBNO at -80°C in heptane. The three lines are labeled by ^{14}N magnetic spin quantum numbers m_I. Low magnetic field modulation width can discriminate other hyperfine components due to the ^{13}C and ^{15}N nuclei. The ^{14}N hyperfine coupling constant at this temperature was a_N= 15.00 G* and it showed a little positive dependence on temperature. The value a_N=15.2 G has been reported in benzene near room temperature.$^{8)}$

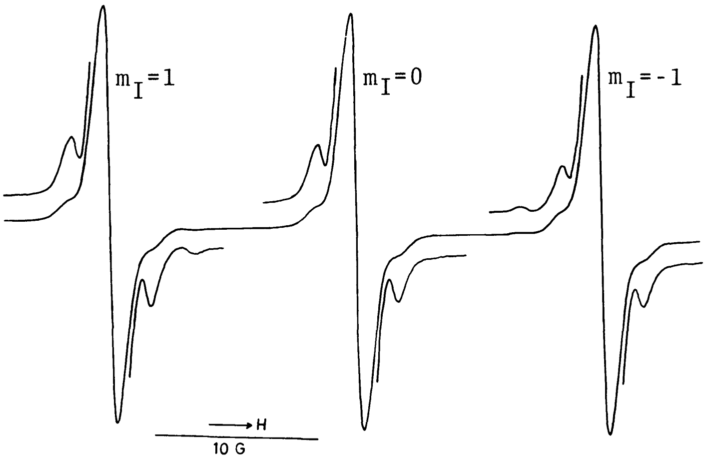

Figure 1 ESR spectrum of DTBNO at -80°C in heptane.

The ^{14}N ENDOR spectra are shown in Fig. 2, where differences in the ENDOR spectra are observed depending on which ESR hyperfine line is monitored. The spectra were obtained at -104°C in heptane but a better signal-to-noise ratio seems to exist in a little higher temperature region. The microwave power was of the order of 80 mW incident on a cylindrical TM_{110} cavity. When the magnetic field is on the cental ESR line (m_I=0), the two ENDOR lines appear at 20.208 and 22.474 MHz with relatively a little stronger intensity in the high frequency line. This amount of inequality in the two ^{14}N ENDOR lines saturating the central ESR line has been reported in other

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* 1 G=0.1 mT.

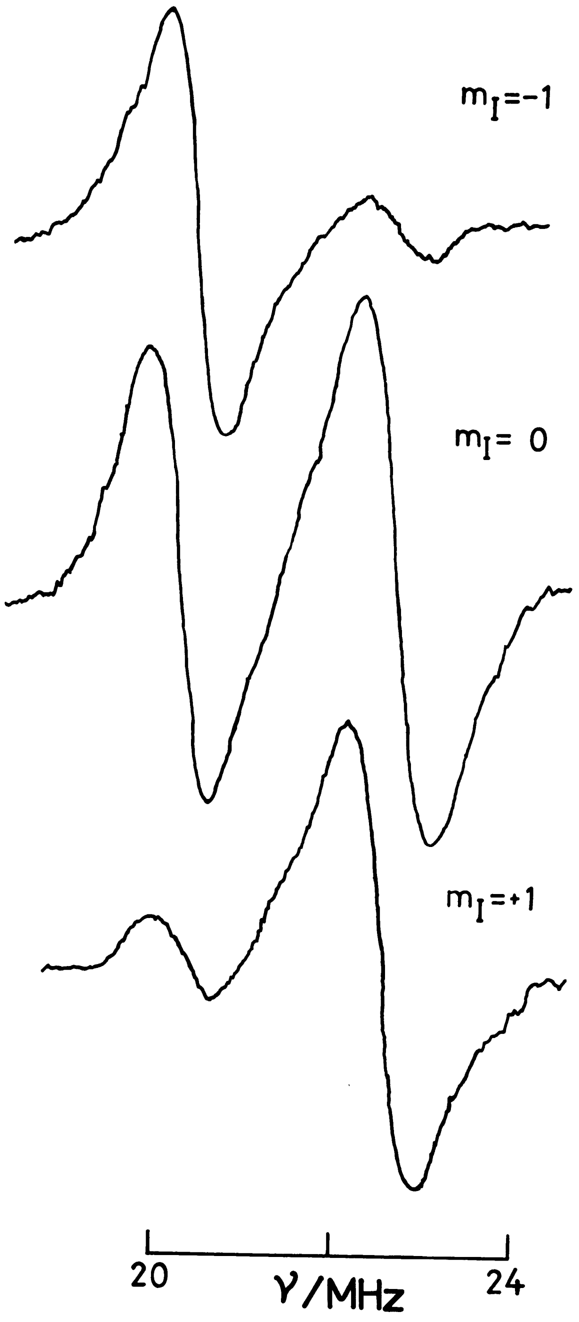

Figure 2 ENDOR signals observed with the magnetic field on each of the ESR lines.

systems.[2,6)] This would be attributed to the different effective rf fields at the high and low ENDOR transition frequencies. A simple physical picture describing this enhancement is given by Geschwind.[9)] The average frequency value of the two ENDOR lines, which should be equal to half of the nitrogen hyperfine coupling constant, corresponds to a_N=15.20 G in good agreement with the experimental value. On the other hand, the difference between the two ENDOR frequencies is usually equal to the nuclear resonance frequency of nitrogen atom at the experimental magnetic field. This difference (2.266 MHz) is larger by 10 % than the nitrogen nuclear resonance frequency estimated to be 2.058 MHz at the present experimental conditions. This kind of discrepancy was first observed in alicyclic nitroxides, indicating second order shifts of the nitrogen hyperfine lines described by the six level system with S=1/2 and I=1. DTBNO shows almost the same value as is observed for TANONE radical (2.260 MHz) because of the nearly same value of the nitrogen hyperfine coupling constant (14.34 G for TANONE). The second order shifts are also responsible for the slight different resonance frequencies and the unequal spacings observed when the magnetic field is on the high field (m_I=-1) and on the low field (m_I=1) ESR lines, as is shown in Fig. 2.

The observed ENDOR intensities evidently show an important role of cross relaxation when the magnetic field of monitoring ESR is changed. In the case of the magnetic field on the high field ESR line (m_I=-1), the low frequency ENDOR line is about 5 times stronger than its high frequency partner. This situation is completely reversed when the magnetic field is on the low field ESR line (m_I=1). Two lines of almost equal intensity are observed when the central ESR line ($m_I=0$) is monitored. These ENDOR intensity changes can be explained by assuming unequal cross relaxation rates between the electron and nuclear spin levels.2)

Appreciable proton ENDOR signals could not be detected so far in spite of the fact that proton signals are also observed in the alicyclic nitroxide radicals with intensities roughly the same as those from the nitrogen. We have no explanation about this result at present but one of the reasons may be that the optimum conditions for observing the proton signals are quite different from those for the nitrogen because of the additional degrees of freedom in molecular motions for DTBNO as compared to the alicyclic nitroxides. Effort is now being made to find the proton signals.

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