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GENERAL TRIPLE RESONANCE OF DIPHENYL NITROXIDE

Yasuo DEGUCHI, Keiichi OKADA, Jun YAMAUCHI,* and Kanae FUJII†
College of Liberal Arts and Sciences, Kyoto University, Kyoto 606
† Japan Electron and Optics Laboratory Co. Ltd., Akishima, Tokyo 196

General triple resonance spectra of diphenyl nitroxide have been observed in ethylbenzene at -90°C by means of the ENDOR spectrometer with a TM_{110} mode cavity. The signal intensity was greatly influenced by the pumping frequency set on each of the ENDOR lines. The results indicate that two hyperfine couplings of the meta and para or ortho positions have opposite signs.

An extension of electron-nuclear double resonance (ENDOR) to triple resonance has been discussed in detail[1)] and the following two methods have been established; special triple resonance and general triple resonance. There are two characteristics in these techniques, that is, signal enhancement and sign determination of hyperfine coupling constants. However, reports on the triple resonance of free radicals in solutions are very few. This paper is a short communication of general triple resonance on diphenyl nitroxide (DPNO) in ethylbenzene at -90°C.

The general triple resonance apparatus consists of a JEOL FE-3X spectrometer with a TM_{110} mode cavity and a couple of signal generators, *i.e.* HP8601A (Hewlett-Packard) and VP-8179B10 (National). The former is used for scanning of rf frequency with FM modulation and the latter for pumping of rf frequency without FM modulation. Moreover, a power combiner is employed to combine the pumping and scanning rf powers. Except the pumping rf part the system is the same as is used in ^{14}N ENDOR study of di-*t*-butyl nitroxide.[2)]

ESR investigations of DPNO were first made in solid[3)] and in solution.[4)] DPNO shows two isotropic hyperfine couplings a_1=1.91 and a_2=0.82 G[††] in ethylbenzene. These are assigned to six equivalent protons at the para and ortho positions

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[††] 1 G = 0.1 mT in SI units.

and four equivalent protons at the meta positions, respectively. The signs of these coupling constants have been determined earlier by anisotropic ESR spectra.[3] Figure 1 shows unpaired-electron distributions calculated by Hückel molecular orbital methods with and without a spin correlation. The spin correlation consideration gives rise to a negative spin density at the meta positions of both benzene rings. Thus, the hyperfine coupling constants are expected to have opposite signs at the meta and para or ortho positions.

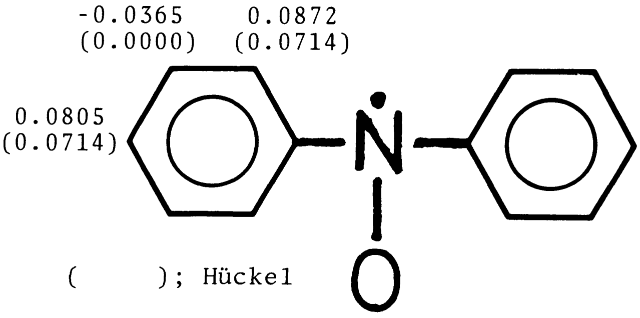

Fig. 1. Spin density distributions by simple Hückel and McLachlan methods.

The upper part of Fig. 2 shows the entire ENDOR spectrum in ethylbenzene at -90°C extending from 11 to 18 MHz. The hyperfine coupling constants determined from ENDOR are $a_1=1.91_3$ and $a_2=0.82_1$ G in excellent agreement with those from ESR. On referring to the molecular orbital calculation, the smaller coupling is assigned to the meta protons which have a negative spin density.

The lower part of Fig. 2 shows the two general triple resonance spectra obtained by pumping the 16.881 and 15.348 MHz lines, respectively. The pumping power is 50 W, while the scanning power is also held on the same level of 50 W as in the ENDOR spectrum shown above. In the case of the upper triple spectrum where the 16.881 MHz line is pumped, the low frequency counterpart of this line is enhanced. The two lines belonging to the other group of nuclei, on the other hand, show a contrary behavior such that the low frequency line is de-enhanced while the high frequency line is enhanced. In the general triple resonance spectrum where the 15.348 MHz line is pumped, this intensity behavior is entirely reversed. Not shown are the general triple resonance spectra in which the low frequency lines at 13.044 and 11.512 MHz are pumped. In these cases the intensity patterns are simply mirror images of the former spectra with respect to the free proton frequency.

Using the theoretical results by Möbius *et al.*[1] one can understand these properties as follows. In the general triple resonance spectrum where the 16.881 MHz line is pumped, the signal intensity at 13.044 MHz is reduced, that is, $V<1$, where V is a ratio between triple and ENDOR signal intensities. This means that

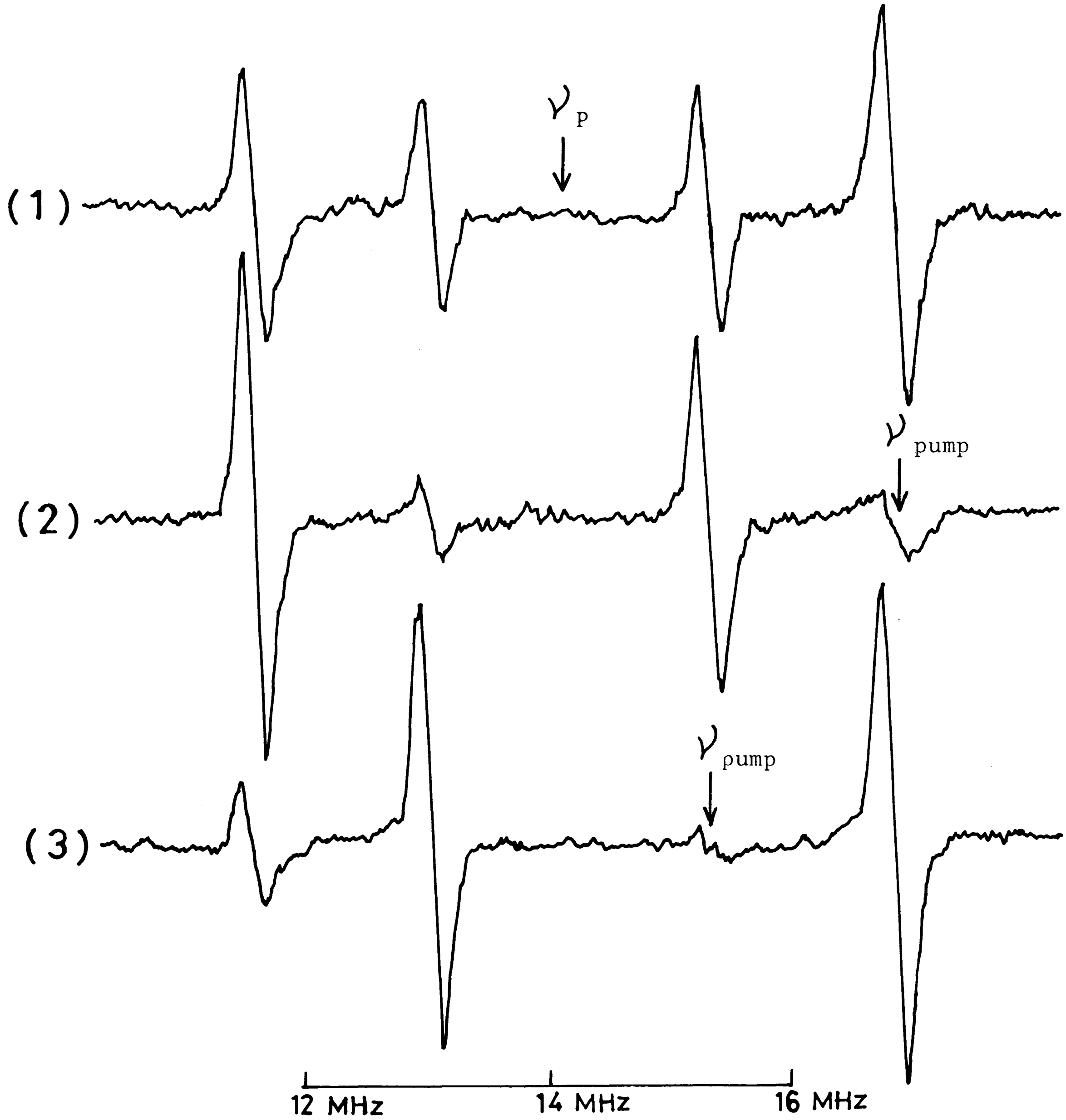

Fig. 2. ENDOR spectrum (1) and general triple resonance spectra (2) and (3) in ethylbenzene at -90°C. The arrows indicate free proton frequency (ν_p) and pumping frequency (ν_{pump}).

a pyramid experiment in Möbius' textbook[1)] is just performed. As a result, its high frequency counterpart at 15.348 MHz responds according to a tetrahedron experiment, implying V>1. For the low frequency counterpart of the pumped line one always expects an enhancement because this is the case of special triple experiment. Next let us see the general triple spectrum where the 15.348 MHz line is pumped. The low frequency line at 11.512 MHz can be referred to a pyramid case while its high frequency counterpart corresponds to a tetrahedron experiment. The partner of the pumped line is again enhanced. These relations between signal enhancement and de-enhancement or between pyramid and tetrahedron experiments are understandable on the basis of different signs of the two hyperfine coupling constants.¹⁾

Thus, one can finally conclude that the two coupling constants a_1 and a_2 of DPNO have opposite signs in agreement with the earlier results.

A more detailed report with respect to the general triple resonance of DPNO will be published in due course.

References

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