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An ENDOR Study of Diphenyl Nitroxide and Its Methyl Derivatives, The Effect of the Methyl Substitution

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The ENDOR spectra of diphenyl nitroxide (DPNO) and its monomethyl derivatives were observed in ethylbenzene at −70 °C. The agreement between the ESR and ENDOR data is generally good. The MO calculations, however, indicate a few disagreements in the case of the *m*- and *o*-methyl DPNO derivatives. The methyl substitution at the meta-position destroys the equivalency of all protons at the meta-positions, which are divided into two sets of equivalent proton groups of the same number. The ortho-substitution weakens the coplanarity of the two benzene rings and increases the number of the equivalent proton groups, which are fully resolved in the ENDOR spectrum. The steric hindrance is taken into account in the MO calculation, which can predict these slightly different coupling groups-again except for those in the meta-positions. A satisfactorily simulated spectrum of the *o*-methyl DPNO is obtained on the basis of the ENDOR data.

Previously two of the present authors (J.Y. and Y.D.) have investigated the hyperfine structures of several neutral radicals by means of the electron spin resonance (ESR).[1)] In this work, diphenyl nitroxide (DPNO) and its methyl derivatives have been discussed in detail from the point of view of steric effect. The hyperfine coupling constants of the nitrogen and protons have been greatly affected in the case of the ortho-substituted compounds. The steric hindrance has weakened the coplanarity of the two benzene rings and caused a redistribution of the spin density such that the number of the equivalent proton group is increased, giving rise to complex ESR spectra. This must be one of the reasons why the ESR spectra of the ortho-methylated compounds could not be analyzed completely, whereas unambiguous analyses and assignment have been done for the other derivatives.

Electron nuclear double resonance (ENDOR) is the most useful for establishing the detailed proton hyperfine coupling constants in complicated ESR spectra.[2)] Thus, the application of the ENDOR to the methylated DPNO derivatives was attempted in order to confirm the steric effect of the ortho-substituted compounds. As far as we know, there has been no such ENDOR work, not even on the parent compound DPNO. Thus, in this paper a proton ENDOR study is reported on DPNO and its monomethyl derivatives, with an emphasis placed on the *o*-methyl DPNO; the effect of the methyl substitution is also discussed.

Nitroxide radicals have previously been investigated extensively by means of ENDOR. For example, there are several works on the neutral nitroxide radicals containing aliphatic and/or aromatic substituent;[3—7)] also the ^{14}N-ENDOR of the nitroxides is another interesting subject.[8—12)] ESR investigations of DPNO have been made in a solid[13)] and in solution.[1)] DPNO shows two isotropic hyperfine coupling constants $A_1=1.91$ and $A_2=0.82$ G ($1\text{ G}=10^{-4}\text{ T}$) in ethylbenzene.[14)] These are assigned to the six equivalent protons at the ortho- and para-positions, and to the four equivalent protons at the meta-positions, respectively.[1)] The para- or meta-substitution of a methyl group has little influence on the spin density distribution. Thus, the ESR spectra are easily explained by considering the increased proton number on the substituted position. Ortho-substituted DPNO, on the other hand, shows a drastic redistribution of the spin density because of strong bond-twisting.[1)] Recently a short communication about a general triple resonance experiment on DPNO has been published.[14)] The general triple resonance made possible the determination of the relative signs of the hyperfine coupling constants of the protons; that is, the two coupling constants, A_1 and A_2, of DPNO have opposite signs, in agreement with the earlier result.[13)]

Experimental

DPNO and its derivatives are fairly unstable; thus, one should use a radical compound synthesized freshly in order to prepare a sample of its solution. Synthetic methods were described in the previous paper.[1)] Solution samples for ENDOR measurements were prepared by the standard technique, using ethylbenzene as the solvent. The ESR and ENDOR spectra were recorded at −2 and −70 °C respectively for the best resolution.

The ENDOR spectrometer consists basically of a commercial JEOL FE-3X ESR spectrometer, with a JEOL ES EDX2 ENDOR accessory equipped with a TE_{011} cavity. Moreover, a broad-band ENDOR accessory equipped with a TM_{110} was built. This is similar to the one reported previously.[15)] A simple block diagram is shown in Fig. 1. The TM_{110} cavity contains a silver solenoid of 20 turns (30 mm length, 7 mm o.d., made of silver wire 1 mm in diameter) directly mounted on a thin quartz tube; it is supplied with microwave power through a coupling iris which connects the cavity with the wave guide. With this device, it is easier to adjust the coupling between the cavity and the transmission line of microwave power than with the coaxial-line method. A frequency generator (Hewlett-Packard HP8601A) generates the radiofrequency, which passes through a broad-band power amplifier (ENI A300) and the solenoid. Finally, its power is dissipated in a 50 Ω oil-cooled resistor (TRIO RF DUMMY LOAD RD 300). A linear amp simultaneously sweeps the 6.5 KHz FM frequency of the oscillator and drives the *X*-axis of the *X*-*Y* recorder. The phase-sensitively detected changes of the absorbed microwave power generate the signal voltage,

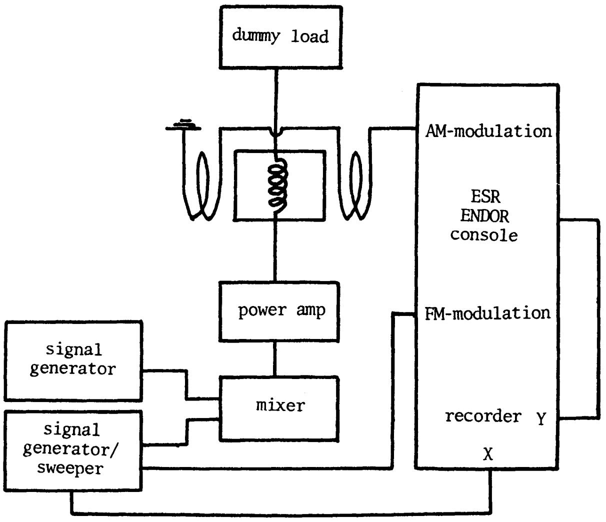


Fig. 1. A block diagram for ENDOR and triple experiments using a TM_{110} mode cavity.

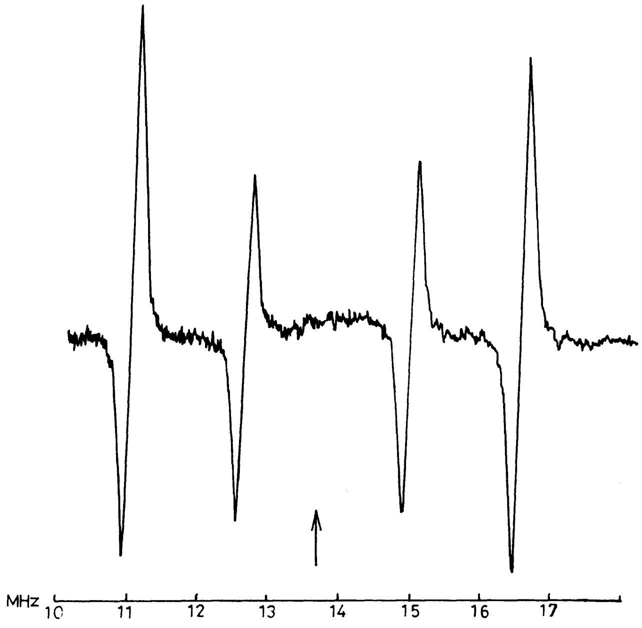


Fig. 2. ENDOR spectrum of DPNO in ethylbenzene at −70°C. The arrow indicates the frequency of free proton.

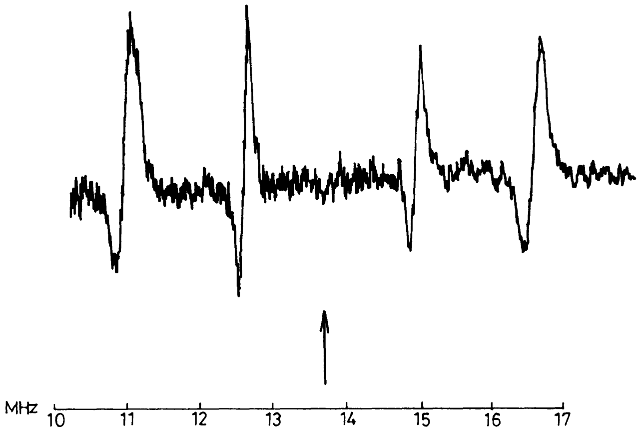


Fig. 3. ENDOR spectrum of *p*-methyl DPNO in ethylbenzene at −70°C. The arrow indicates the frequency of free proton.

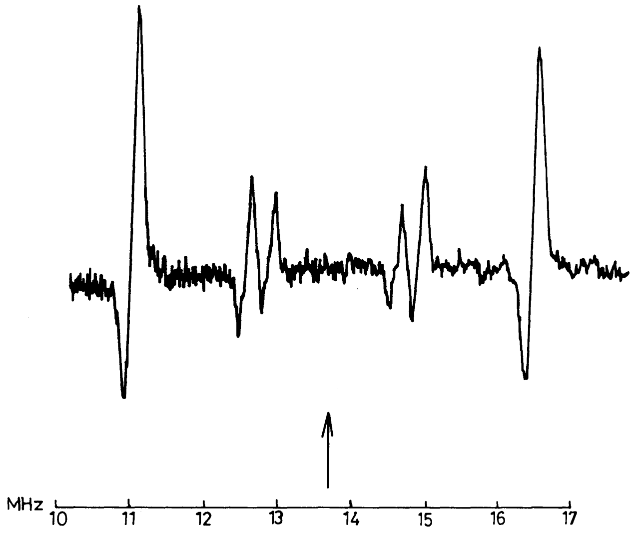


Fig. 4. ENDOR spectrum of *m*-methyl DPNO in ethylbenzene at −70°C. The arrow indicates the frequency of free proton.

driving the *Y*-axis of the recorder. The ENDOR signals are observed in the systems of both TE_{011} and TM_{110} cavities. In the spectra themselves, there are no essential differences. However, the TM_{110} cavity system surely has certain advantages, as has been pointed out elsewhere11,14–16) The ENDOR spectra shown in this paper were all recorded by means of the TM_{110} cavity.

Results

The ENDOR spectrum of DPNO is shown in Fig. 2, from which one can recognize that the protons on both benzene rings are to be classified into two different sets, such as one group of para- or ortho-protons and another group of meta-protons. Features similar to those in DPNO appear in the cases of *p*-methyl and *m*-methyl DPNO (Figs. 3 and 4). The ortho-methylated derivative of DPNO, however, shows a fairly different appearance in its ENDOR spectrum, as is shown in Fig. 5; firstly, the overall width of the spectrum is about 8 MHz, about 2 MHz larger than that of DPNO. Secondly, the weak ENDOR absorption lines due to several sets of equivalent protons can be observed. The proton hyperfine coupling constants determined from the ENDOR spectra are summarized in Table 1, in which the data obtained from the ESR spectra are also listed for comparison. Two of the present authors (J.Y. and Y.D.) could not analyze the ESR spectrum of the *o*-methyl DPNO, but at this time the ESR spectral analysis could be made on the basis of the ENDOR results and the spectrum could be simulated using the hyperfine coupling constants listed in the table.

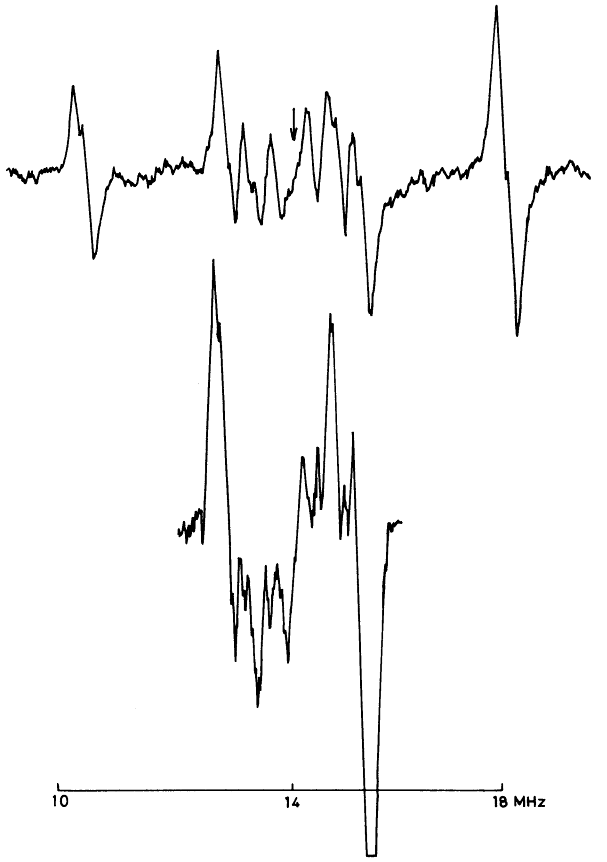
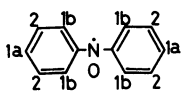
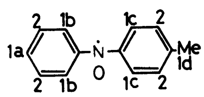
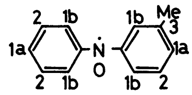
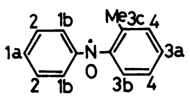


Fig. 5. ENDOR spectrum of *o*-methyl DPNO in ethylbenzene at −70°C. The arrow indicates the frequency of free proton. The central part of higher sensitivity and resolution is also shown.

Discussion

The agreement between the ESR and the ENDOR data is excellent, except in the case of *o*-methyl DPNO. For further comparison, the usual MO calculations were performed. The same MO parameters as in the previous paper were employed for the simple Hückel and McLachlan methods. Thus, the theoretically calculated hyperfine coupling constant in each position is also shown in Table 1, where the McConnel relation between the spin density and the hyperfine coupling constant is applied with a proportionality constant of $|Q|=27.3$ G. The calculations also support the assignment which has been made mainly on the basis of the ESR simulation. Here a comment about *m*-methyl DPNO is appropriate. In this radical, both ESR and ENDOR assure two kinds of equivalent proton sets in the meta-positions. The inner pair of absorption lines in DPNO and its *p*-methyl derivative splits into two lines *m*-methyl DPNO, giving 814 and 577 mG splittings. These are also ascertained by the ESR simulation; 810 and 580 mG. However, the equivalent proton numbers of both hyperfine coupling constants are found to be the same, so that there is no way to assign the larger hyperfine coupling to the methyl or the other meta-protons. Deuteron substitution (for example, trideuteriomethyl substitution at the meta-position) would be necessary to solve this problem. On the other hand, the MO calculation predicts only a minor difference, less than 30 mG, between

Table 1. ESR, ENDOR, and MO Calculation Results for DPNO and Its Derivatives

Compound		A_{H1}/G	A_{H2}/G	A_{H3}/G	A_{H4}/G	A_{N}/G
	ESR	1.910	0.820			9.500
	ENDOR	1.914	0.817			—
	cal[a]	a 1.966	0.938			9.500[c]
		b 2.153				
	ESR	1.890	0.830			9.750
	ENDOR	1.980	0.834			—
	cal[a]	a 1.980	0.932			9.525[c]
		b 2.167				
		c 2.148				
		d 1.896				
	ESR	1.920	0.810	0.580		9.580
	ENDOR	1.923	0.814	0.577		—
	cal[a]	a 1.966	0.938	0.910		9.503[c]
		b 2.156				
	ESR	2.680	0.830	0.560	0.280	9.941
		2.610		0.500		
	ENDOR	2.731	0.881	0.600	0.249	—
	cal[b]	a 2.405	1.226	a 0.552	0.305	10.440[c]
		b 2.691		b 0.647		
				c 0.608		

a) A twisted angle of 45° is assumed. b) A twisted angle of 60° is assumed. c) A proportionality constant of $|Q|=27.3$ G is assumed so that the DPNO value is reprodued.

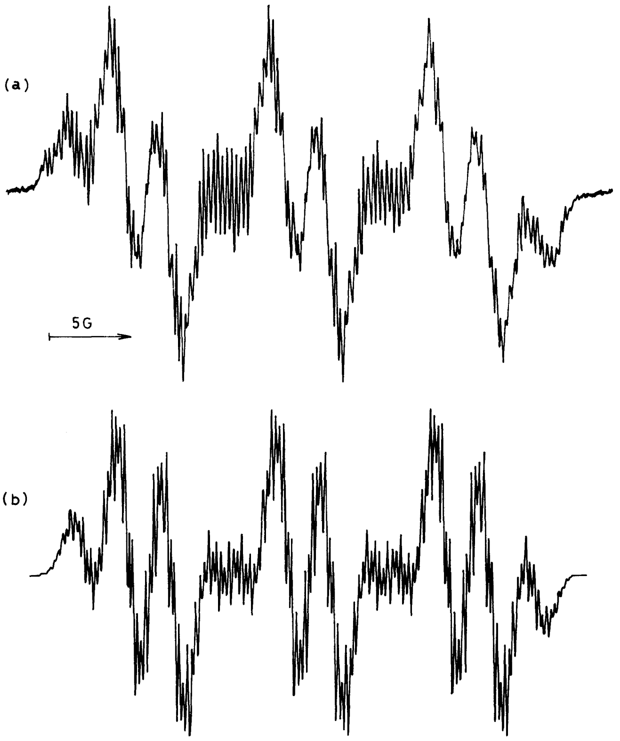


Fig. 6. ESR(a) and simulated(b) spectra of *o*-methyl DPNO.

these positions. We have no reasonable explanation about this discrepancy at present. In Table 1, therefore, the larger hyperfine coupling constant is assigned temporarily to the *m*-methyl protons, following the MO calculation.

The fact that the overall width of the ENDOR spectrum of *o*-methyl DPNO is larger than that of DPNO implies that the steric hindrance effect of the methyl group substituted at the ortho-position of the benzene ring is dominant in this case; that is, there is a greater population of electron on the N-O bond and the benzene ring of no-methyl substitution than on the twisted tolyl ring. In the earlier ESR, only the biggest proton coupling (2.70 G) was recognized except for the nitrogen one, which gave a quartet appearance in the spectrum (Fig. 6). A similar value, although the absorption line is slightly split, is also observed this time in the ENDOR spectrum (Fig. 5), from which three additional sets of equivalent protons are revealed in the smaller splitting groups. In a more highly sensitive spectrum, it seems that the smaller two groups split into two splittings further, as is shown in Fig. 5. All these slightly different values obtained experimentally can be predicted by the theoretical MO calculations, assuming the sterically hindered rotation of one phenyl ring containing the substituted methyl group away from the remaining π-electron framework, which includes the N-O nitroxide group. This assumption has been discussed in detail in the previous paper,[1] where a twisted angle of 55—60° was anticipated for a proton-methyl proton repulsion case. In Table 1 the results of the MO calculation (a twisted angle of 60° is assumed) are compared with the experimental results; the fit is excellent except for the second biggest proton coupling, which is assigned to the meta-positions of the unsubstituted benzene ring. Considering the tendency of the other protons, it is rather difficult to understand this value. The steric hindrance makes the unpaired electron highly populated on the ortho- and para-positions of the unsubstituted benzene ring. Nevertheless, the meta-proton hyperfine coupling constant increased less than 10%, whereas a 40% increase is observed in the para- and ortho-positions. On the other hand, the MO calculations show that all positions of the unsubstituted benzene ring are equally influenced to localize the unpaired electron ca. 40% more and that the calculated hyperfine coupling constants, except for this meta-position, are in good agreement with the experimental values. This quantitative singularity at the meta-position, together with the discrepancy discussed in the *m*-methyl DPNO, may be relevant to a special characteristic of the meta-positions of the benzene rings, that is, a negative spin density. A more sophisticated MO treatment and/or steric hindrance mechanism is necessary. This will be commented on in the Discussion section later. At any rate, the comparatively good agreement surely supports the validity of the steric hindrance mechanism developed in the earlier paper.[1]

The ESR simulation was carried out on the basis of the ENDOR results. DPNO and its *p*-methyl derivative are straightforward, and the *m*-methyl DPNO is almost the same. Even a stick-diagram construction can yield reliable values. It is found that the coupling constants of the *m*-methyl DPNO, 810 and 560 mG, which are assigned to the meta-positions, should be taken into account so as to produce quartet splittings. This means that three protons in each group should contribute as an equivalent proton group. Then the well-simulated spectrum can be reproduced. The assignment, however, is still ambiguous, although it is narrowly evidenced by the MO calculation. For the *o*-methyl DPNO, there are many sets of equivalent protons so that the assignment seems to be really intuitive for the smaller coupling groups. According to the MO calculation, however, the magnitude of the hyperfine coupling constants agrees well with the experimental values; thus, one can assign each hyperfine coupling so as to satisfy the order of its magnitude. Furthermore, if one takes into account several experimental facts, for instance, the facts that the ortho- and para-proton hyperfine coupling constants are almost equal and are bigger than the meta-protons, or that the unpaired electron is highly localized on the unsubstituted benzene ring, the analysis can be nearly perfect. By changing the coupling constants little by little from the ENDOR values we finally come to the simulated spectrum shown in Fig. 5. Of course, a minor modification would still be necessary to complete it. Generally speaking, however, the ESR data of the sterically hindered *o*-methyl DPNO in Table 1 are considered to be reasonable.

The general triple resonance of DPNO was described in an earlier communication,[14] where it was clarified that the two hyperfine coupling groups of the meta- and para- or ortho-positions have opposite signs. Usually one may assume a positive spin density on the carbon atoms at the para- and ortho-positions and, therefore, a negative spin density at the meta-positions, as has been evidenced by several MO calculations. This means that the spin density on the carbon atoms at the meta-positions is rather small but, on the contrary, is easily influenced by many factors, for example, MO parameters, substituents, steric rotations, and solvents. Therefore, the discrepancy and the singularity observed in the meta-positions in this experiment may be attributed to these properties. To solve the problem, more precise work, such as deuteron substitution, a study of the solvent effect, and triple experiments for the methylated DPNO, will be necessary.

In conclusion, the ENDOR study supports the previous ESR work. In the para- and meta-methylated DPNO, only a few modifications of DPNO are necessary; that is, the methyl substitution in such positions results in little change in the spin density distribution. The ortho-methylated DPNO is twisted at one N–C bond, which is attached to the substituted benzene ring. The data calculated on the assumption that the twisted angle is 60° are reasonable and consistent with the spin density distribution and the steric hindrance consideration discussed previously.[1] We observed a minor but clear discrepancy and singularity in the meta-positions of the meta- or ortho-substituted DPNO.

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