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Electron Spin Resonance Studies of Diphenyl Nitric Oxide Derivatives

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A series of diaryl nitric oxide radicals have been studied by the use of the electron spin resonance (ESR) technique. Several methyl derivatives of diphenyl nitric oxide were synthesized and their ESR spectra investigated. It has been shown that the hyperfine coupling constants of ^{14}N, especially those of protons, are much affected in the case of the ortho-methylated compounds as a result of steric hindrance, which is discussed using the Hückel molecular-orbital theory and the valence-bond theory. In conclusion, two benzene rings of diphenyl nitric oxide derivatives are equivalently distorted for the symmetrically-substituted compounds and unequivalently for the unsymmetrically-substituted compounds. Furthermore, this tendency is strengthened by ortho-substitution.

Many investigators have previously studied various kinds of neutral free radicals by means of the ESR method. Some of these radicals have been those of alkyl or aryl derivatives of nitric oxide. Since they are not as stable as diphenyl picryl hydrazyl (DPPH), however, there have been few results of the investigation, and the experiments have been carried out by the reaction of corresponding amines or hydroxylamines with the appropriate oxidants in the various systems.[1] However, many new stable radicals of nitric oxide derivatives have recently been found.[2]

Some of the present authors have previously reported on ESR studies of diphenyl nitric oxide (DPNO) in a solid state[3] and in a liquid solution,[4] and of di-*p*-anisyl nitric oxide, a dimethoxy derivatives of DPNO, in a liquid state.[5] Similarly, the ESR spectra of methyl-substituted DPNO have been reported.[6] However, there have been no detailed ESR studies of methyl-substituted DPNO.

We have now observed the proton hyperfine spectra of *p*-, *m*-, *o*-methyl diphenyl nitric oxide (tolyl phenyl nitric oxide), *p,p′*-, *m,m′*-, *o,o′*-dimethyl diphenyl nitric oxide (ditolyl nitric oxide), *p,o′*-dimethyl diphenyl nitric oxide, *p,o,o*-trimethyl diphenyl nitric oxide (mesityl phenyl nitric oxide), and *p,o,o,p′*-tetramethyl diphenyl nitric oxide (mesityl tolyl nitric oxide) in liquid solutions and have studied the effect of methyl substitution on the spin density distribution on nitrogen and ring-carbon atoms. The steric influences of substituents have been reported in many regions of ultraviolet spectroscopy, infrared spectroscopy, and electron diffraction. The steric effect has also been observed in ESR studies of several ortho-substituted radicals.[7-9] DPNO derivatives which contain methyl groups in ortho-positions have a similar effect and a remarkable change in spectra is also observed in them; this change has been attributed to the forced internal rotation of the phenyl ring resulting from the steric repulsion between two ortho-groups. We will also discuss our findings in terms of the steric repulsion energy and the resonance energy from the view point of molecular-orbital calculation and the valence-bond theory. Finally, the solvent effect will be discussed.

Experimental

DPNO and its derivatives were synthesized by following the method of Wieland and Roth.[10] Some were crystallized, and some were not. They were oxidized in vacuum-sealed glass tubes by silver oxide (Ag_2O) from the corresponding hydroxylamines, which are also unstable. The spectra were usually recorded below room temperature in order to get the most highly-resolved ESR spectra. The solvents, the ESR spectrometer, and the reference for observing the hyperfine

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[1] R. H. Hoskins, *J. Chem. Phys.*, **25**, 788 (1956); J. C. Baird and J. R. Thomas, *ibid.*, **37**, 1879 (1961); J. Q. Adams, S. W. Nicksic and J. R. Thomas, *ibid.*, **45**, 654 (1966); H. Lemaire, Y. Marechal, R. Ramasseul and A. Rassat, *Bull. Soc. Chim. France*, **1965**, 372.

[2] A. K. Hoffmann and A. T. Henderson, *J. Am. Chem. Soc.*, **83**, 4671 (1961); W. D. Blackley and R. R. Reinhard, *ibid.*, **87**, 1802 (1965); M. B. Neiman, E. G. Rozantzev and Yu. G. Mamedova, *Nature*, **196**, 476 (1965).

[3] Y. Deguchi, This Bulletin, **34**, 910 (1961).

[4] Y. Deguchi, *ibid.*, **35**, 260 (1962).

[5] K. Umemoto, Y. Deguchi and H. Takaki, *ibid.*, **36**, 560 (1963).

[6] E. G. Rozantzev, *Uspeki Khimii*, **35**, 1549 (1966).

[7] K. Maruyama, R. Tanikaga and R. Goto, This Bulletin, **36**, 1141 (1963).

[8] K. Ishizu, *ibid.*, **37**, 1093 (1964).

[9] H. R. Falle and F. C. Adam, *Can. J. Chem.*, **44**, 1387 (1966); H. R. Falle and F. C. Adam, *ibid.*, **44**, 1397 (1966).

[10] H. Wieland and K. Roth, *Ber.*, **53**, 216 (1920).

coupling constants were the same as in the case of DPNO.⁴⁾ The experiments have already been described in detail elsewhere.⁴,⁵⁾

Results and Discussion

Analysis of the ESR Spectra. The observed spectra always consist of three well-resolved groups, arising from the interaction of the unpaired electron with a nitrogen nucleus (^{14}N), if a proper radical concentration is maintained. Each of the three groups splits further into many fine absorption lines as a result of the interaction with the proton nuclei. The coupling constants obtained are summarized in Table 1. For instance, Fig. 1 shows the ESR spectrum of *p, p'*-dimethyl DPNO in carbon tetrachloride.

The absorption lines of all the compounds show the effect of the anisotropy of the molecular motion in a solution,¹¹⁾ which results in a different line width for each line, as can be seen from Fig. 1, much as in the case of DPNO.⁴⁾ The analysis of the spectra is quite straightforward for para- and meta-substituted diphenyl nitric oxide. The ESR spectra of these compounds can be completely analyzed by considering the following two assumptions: 1) the proton coupling constants of ortho- and para-positions are the same, and 2) the introduction of a methyl group into the para- or meta-positions leads only to an increase in the number of components of the spectrum, without any change in the coupling constants. The first assumption is reasonable, considering the investigation of a deuterized DPNO⁴⁾; both assumptions are also confirmed by the theoretical estimates of the spin density distribution. However, the compounds 3 and 7 in Table 1 require a modification of these assumptions; that is, the coupling constants of methyl protons in meta-positions are not equal to those of meta-protons, but are slightly larger. A similar case is the symmetrically ortho-substituted DPNO (compound 8 in Table 1). In this case the coupling constants of methyl protons in ortho-positions are larger than those of the other ortho- and para-protons.

A quite different result is obtained on introducing the methyl groups into ortho-positions unsymmetrically. Then each component of the nitrogen triplet is split into four main lines, with a ratio of intensities of 1 : 3 : 3 : 1. Compound 4 in Table

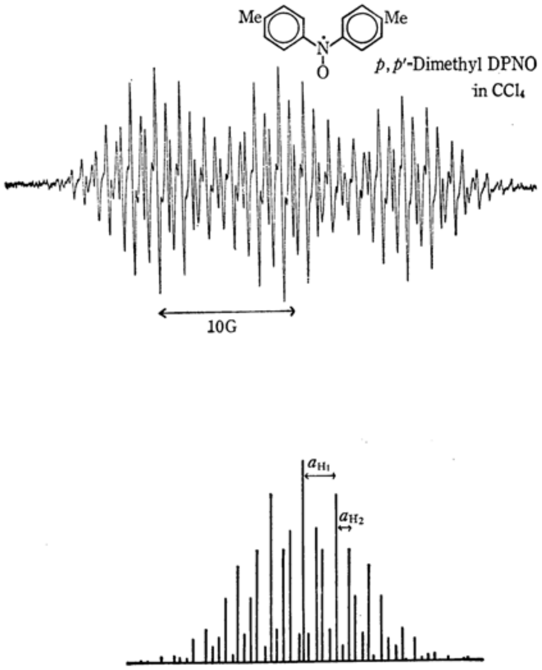

Fig. 1. ESR spectrum of *p, p'*-dimethyl DPNO in carbon tetrachloride and constructed spectrum with experimentally determined coupling constants. Constructed spectrum is one group of nitrogen triplet.

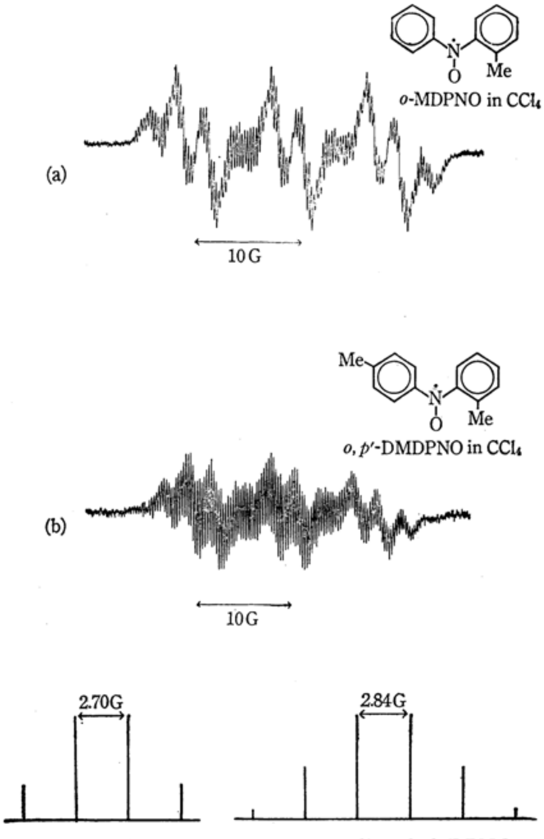

Fig. 2. ESR spectra of (a) *o*-methyl DPNO and (b) *o, p'*-dimethyl DPNO in carbon tetrachloride. (c): Schematic diagram of proton hyperfine spectra of *o*-methyl DPNO and *o, p'*-dimethyl-DPNO. This is one group of nitrogen triplet.

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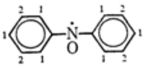
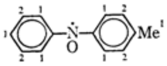
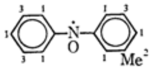
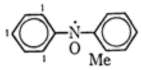
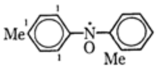
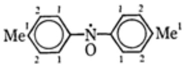
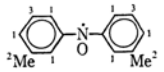
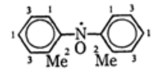
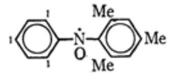
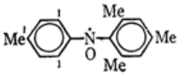
11) H. M. McConnell, *J. Chem. Phys.*, **25**, 709 (1956); D. Kivelson, *ibid.*, **33**, 1094 (1960).

Table 1. Coupling constants of DPNO and its related compounds in carbon tetrachloride (in Gauss)

A_N	A_{H1}	A_{H2}	A_{H3}	Compound
9.50	1.90	0.85		 1
9.59	1.80	0.80		 2
9.58	1.84	0.77	0.58	 3
9.81	2.70	1.0>		 4
9.84	2.84	1.0>		 5
9.76	1.95	0.85		 6
9.72*	1.85*	0.75*	0.55*	 7
10.50*	1.00*	1.50*	0.16*	 8
10.05	2.84	~0.8		 9
10.10	2.84	~0.8		 10

Coupling constants A_{H1}, A_{H2} and A_{H3} are assigned to the protons 1, 2 and 3 respectively labeled to the compound formula. * Values in tetrahydrofuran (Mr. Nakata's data)

1 is an instance; its ESR spectrum is shown in Fig. 2-a. In order to ascertain which protons cause this interaction of quartet splitting, we synthesized the compound 5 in Table 1 and observed the ESR spectrum, which is shown in Fig. 2-b. From these two spectra it can be said that para-methylation in the compound 4 makes the four main lines with an intensity ratio of 1 : 3 : 3 : 1 change into the six main lines with an intensity ratio of 1 : 5 : 10 : 10 : 5 : 1, and changes the coupling constant from 2.70 G to 2.84 G. This is schematically illustrated in Fig. 2-c. Therefore, by considering the above two assumptions, the quartet splitting of the compound 4 is assigned to one para- and two ortho-protons of one benzene ring which is not ortho-methylated, and sextet of the compound 5, to the protons of para-methyl and two ortho-protons of one benzene ring.

This is also true for the compounds 9 and 10, whose ESR spectra are shown in Fig. 3-a and Fig. 3-b respectively. The hyperfine coupling constants of further splittings of the other hydrogen atoms can not be assigned unequivocally.

MO Calculations. In attempting to account for the observed hyperfine coupling constants or spin densities, most authors have used the Hückel molecular-orbital theory, which contains a number of parameters, that is, α's and β's. These parameters have freely been chosen, to some extent, in order to get the best fit with the observed spin densities. We have used the simple Hückel theory to calculate the spin densities of DPNO derivatives, and have made a comparison with the observed values, using the same α and β values throughout all the compounds. Although the present calculations are of a very approximate nature, they allow us to derive some qualitative conclusions recording the observed changes in the hyperfine coupling constants between the compounds.

The simple Hückel theory results in the same spin densities at the ortho- and para-positions, although they cannot predict finite spin densities at meta-positions, which may be negative. In ortho-substituted DPNO, particularly unsymmetrically ortho-substituted DPNO, greater variations are obtained because of the steric effect,

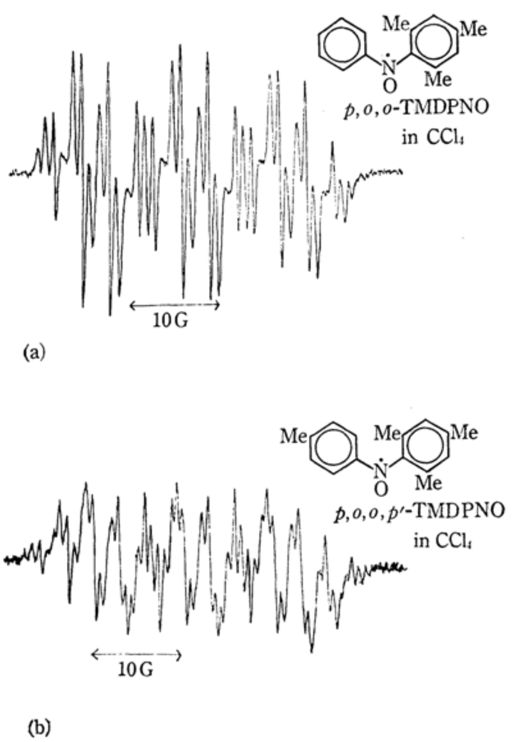


Fig. 3. ESR spectra of (a) *p, o, o*-trimethyl DPNO and (b) *p, o, o, p′*-tetramethyl DPNO in carbon tetrachloride.

as will be discussed below. Some results are shown in Fig. 4. These calculated spin densities agree with the observed values in the ortho- and para-positions if we assume McConnell's first-order formula for the hyperfine coupling constants in aromatic compounds:[12]

$$A_{\mathrm{H}} = Q\rho_c$$

relating the ring proton splitting, A_{H}, with the spin density, ρ_c, in the $2p_z$ orbital of the carbon atom adjacent to the proton, and if Q is set as 23 G, a value determined from the ESR spectra of the methyl radical[13] and the benzene anion radicals at a low temperature.[14] If we apply McLachlan's calculation[15] for the estimation of the spin density distribution in DPNO, a better agreement is obtained. The spin densities of para-, meta-, and ortho-positions become 0.089, -0.029, and 0.091 respectively if we set λ in McLachlan's equation as unity. This calculation indicates that the spin density in the meta-position is negative and agrees with the experimentally-observed value.

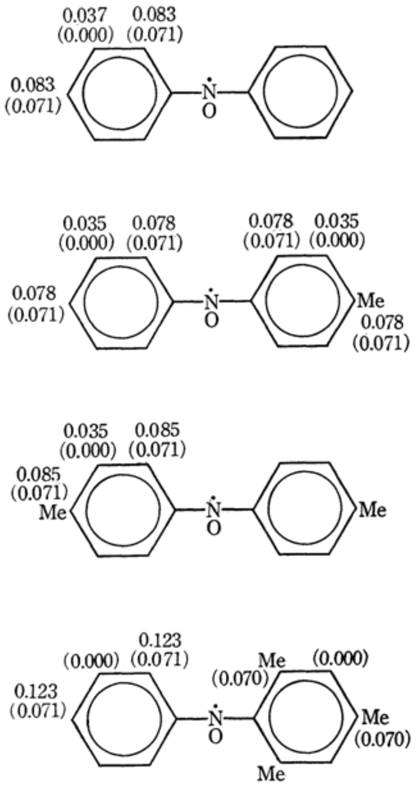


Fig. 4. Observed and theoretically calculated spin densities. Values in parentheses are theoretical.

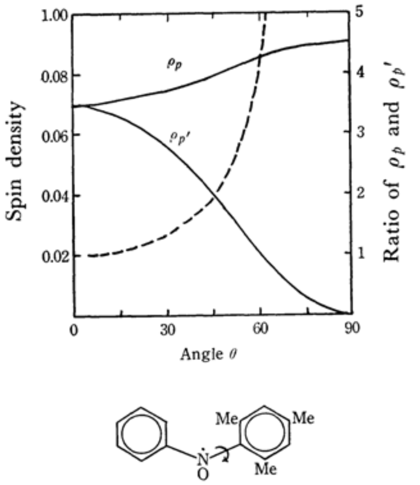


Fig. 5. Angular dependence of spin densities in para-positions and schematic diagram in case of *o, o, p*-trimethyl DPNO. The dashed curve shows the angular dependence of the ratio of ρ_p and ρ_p'.

Steric Effect. Several ortho-substituted radicals have been studied by means of the nuclear hyperfine structure of their ESR spectra.[7,8] In the

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[12] H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956).

[13] R. W. Fessenden and S. Ogawa, *J. Am. Chem. Soc.*, **86**, 3591 (1964).

[14] C. K. Jen, S. N. Foner, E. L. Cochran and V. A. Bowers, *Phys. Rev.*, **112**, 1169 (1959).

[15] A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

radicals of the DPNO type, large variation are observed when bulky methyl groups are substituted into ortho-positions; this variation is drastic when the groups are unsymmetrically substituted, as in the case of benzophenone ketyl.7) Compounds 4, 5, 9, and 10 experience a large localization of the unpaired electron to one benzene ring. This large change can be explained quite well by taking into account the effect of the steric hindrance. In order to confirm the steric effect on the splittings of the ring protons and of the methyl protons, the spin density was calculated with the modification that the resonance integral of the N-C bond was estimated to be $\beta\cos\theta$, where θ is the angle between the $2p_z$ orbitals of the nitrogen (N) and the carbon (C) atoms.

According to the molecular orbital calculation, the distortion at the position of the N-C bond attached to the nonortho-methylated benzene ring localizes the unpaired electron to the ortho-methylated benzene ring, and, conversely, the distortion of the N-C′ bond which is adjacent to the ortho-methylated benzene ring localizes the unpaired electron to the nonortho-methylated benzene ring. Thus, in ortho-substituted DPNO two benzene rings are twisted in a manner resulting in a relatively large N-C′ bond distortion, for the unpaired electron is largely localized to the nonortho-methylated benzene ring, as can be seen from Table 1.

The dependence of the spin density of the ring carbon atoms of the θ angle is shown in Fig. 5 which gives a schematic diagram for the case of *o, o, p*-trimethyl DPNO. As is illustrated in Fig. 5, the spin density (ρ_p) on the para-position of the nonortho-methylated benzene ring is gradually enhanced with an increase in θ's, while, conversely, the spin density (ρ_p') on the other benzene ring is reduced. One may see that the theoretical spin density ratio, ρ_p/ρ_p', approaches the observed proton splitting ratio around $\theta=60°$ if we assume that the coupling constant, A_{H2}, in Table 1 is to be assigned to para-methyl protons.

If we apply this treatment to the case of *o*-methyl DPNO, it can be said that the two benzene rings are twisted by an angle of 50°.

The conclusion that two phenyl rings are twisted each other about 60—50° in these radicals may be confirmed by a discussion of the balance of the steric and resonance energies. First let us begin with a discussion of DPNO; then let us extend this discussion to the compounds 4 and 9. DPNO may have the same molecular structure as *p, p'*-dimethoxy DPNO, whose crystal structure has been determined explicitly.16) With reference to this crystal analysis, the two ortho-hydrogens which are not bonded have overlapping electronic wave functions, so a repulsive energy may exist. This energy can be estimated from the valence-bond theory, which states that the interaction energy, $E(\mathrm{H, H})$, is given by:17,18)

$$E(\mathrm{H, H}) = Q(\mathrm{H, H}) - \tfrac{1}{2}J(\mathrm{H, H})$$

where $Q(\mathrm{H, H})$ is the Coulomb energy and $J(\mathrm{H,H})$ is the exchange energy; that is,

$$Q(\mathrm{H, H}) = \int \varphi_A{}^1(1s)\varphi_A{}^1(1s)\mathbf{H}\varphi_B{}^2(1s)\varphi_B{}^2(1s)d\tau$$

$$J(\mathrm{H, H}) = \int \varphi_A{}'(1s)\varphi_B{}'(1s)\mathbf{H}\varphi_A{}^2(1s)\varphi_B{}^2(1s)d\tau$$

$$\mathbf{H} = 1/R + 1/r_{12} - 1/r_{2A} - 1/r_{1B}$$

where $\varphi(1s)$ represents the 1s orbital of the hydrogen atom; the other subscripts used are illustrated in Fig. 6. Since these two terms, $Q(\mathrm{H, H})$ and $J(\mathrm{H, H})$, are functions of the interatomic distance of two hydrogen atoms, R,19) they can be evaluated as functions of the angle, θ, using the same atomic distances as those of *p, p'*-dimethoxy DPNO, where we must note that the distortion of the N-C bond occurs on both sides of the nitrogen atom equivalently, so that the twisted angle between the two benzene rings is equal to 2θ.

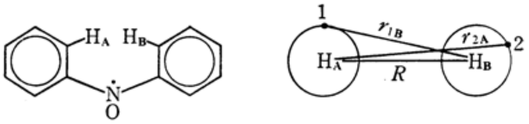

Fig. 6. Repulsion scheme between two ortho-protons.

In this way the ortho-groups can avoid one another and reduce the nonbonding repulsion energy, but this internal rotation is accompanied by an expense of the delocalization energy of the conjugated system. Thus, these two energies being balanced, the configuration may be taken at the minimum point of the sum of these two energies. The delocalization energy of the conjugated system, that is, the resonance energy, can be estimated by either the molecular-orbital theory or the valence-bond theory in a fairly good approximation. Therefore, we calculated the angular dependence of the resonance energy with the simple molecular-orbital theory. The case of DPNO is illustrated in Fig. 7-a, which shows that the benzene rings of DPNO are twisted by an angle of 22.5×2, that is, 45°. According to the analysis of *p, p'*-dimethoxy DPNO, the two benzene rings are tilted approximately 33×2, that is, 66° in the solid state.16)

This same method is applicable to the case of

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16) A. W. Hanson, *Acta Cryst.*, **6**, 32 (1953).

17) C. A. Coulson, "Valence," Oxford University Press, London (1952), Capter 7.

18) M. Cignitti and T. L. Allen, *J. Phys. Chem.*, **68**, 1292 (1964).

19) W. Heitler and F. London, *Zeit. Phys.*, **44**, 455 (1927); Y. Sugiura, *ibid.*, **45**, 484 (1927).

o-methyl DPNO, in which the distortion of the N–C bond occurs only on the side of the benzene ring which is ortho-methylated. The energy diagram is shown in Fig. 8-b, from which it may be concluded that the benzene rings of *o*-methyl DPNO are twisted by an angle of 45—50°; this is nearly the same result as that obtained from the spin density calculation and the experimentally-determined coupling constants.

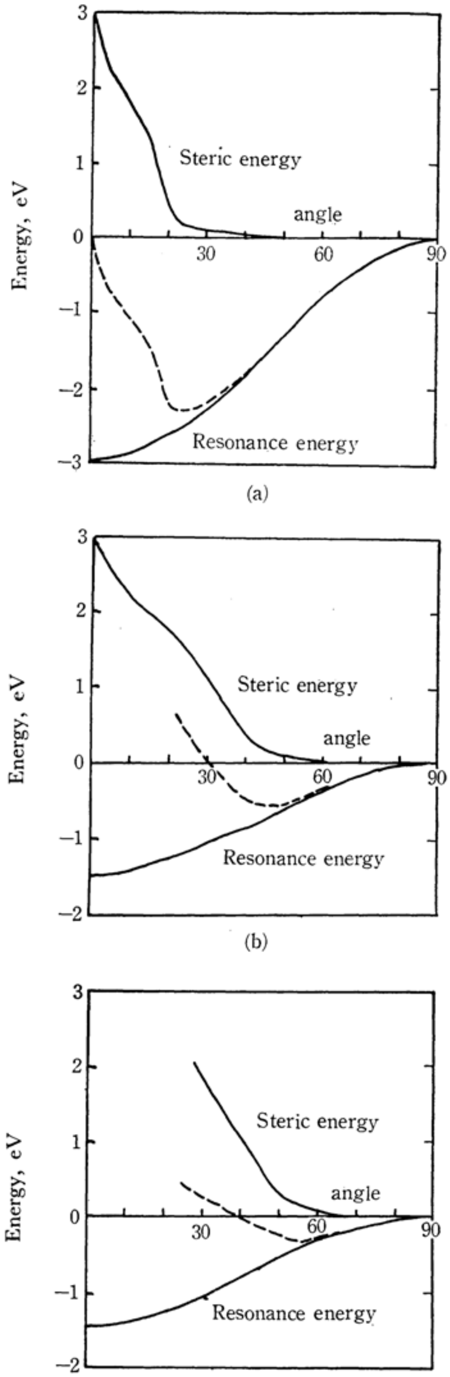

Fig. 7. Steric and resonance energies of DPNO (a), *o*-methyl DPNO (b) and *o, o, p*-trimethyl DPNO (c). The dashed curves indicate sum of these two energies.

This model of steric hindrance can also be applied to the compounds 5, 9, and 10, which are also unsymmetrically ortho-substituted radicals. In the compounds 9 and 10 we assume that the steric energy between ortho-proton and ortho-methyl protons is nearly $3E$(H, H), where E(H, H) is equal to the steric energy of *o*-methyl DPNO, because *o, o, p*-trimethyl DPNO as well as *o*-methyl DPNO has the distorted N–C bond on one side of the nitrogen atom. The similar energy curve for *o, o, p*-trimethyl DPNO is shown in Fig. 7-c, from which the conclusion is obtained that the two benzene rings of *o, o, p*-trimethyl DPNO are distorted about 55°, as is also predicted by the spin density calculation.

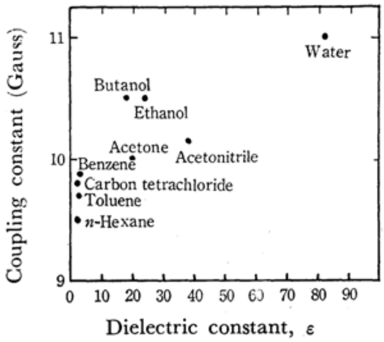

Fig. 8. Solvent effect on the nitrogen hyperfine coupling constant.

In conclusion, in para- and meta-methylated DPNO only a few modifications of DPNO are necessary; that is, methyl-substitution in such positions results in little change in the spin-density distribution. In ortho-methylated DPNO, however, there are two cases: 1) the symmetrically-substituted case, and 2) the unsymmetrically-substituted case, in two benzene rings. In the former case the distortion of the N–C bond occurs equivalently on both sides of the nitrogen atom, and this twisted angle will be of the same order as that of DPNO. The compounds in the latter case are twisted at only one N–C bond, which is attached to the ortho-substituted benzene ring; this twisted angle is about 50°C for a proton-proton repulsion case and about 55—60° for a proton-methyl proton repulsion case.

Solvent Effect. The effect of solvents on the widths of the nitrogen and proton hyperfine coupling constants was found in these radicals in the same way as it was first found in DPNO.4) The nitrogen hyperfine coupling constant increases with an increase in the dipole moments or in the dielectric constants of the solvents. The results obtained in the case of p, p'-dimethyl DPNO are shown in Fig. 8. This solvent effect may be explained qualitatively if we consider the ionic structures of the radical in the valence-bond theory.4) The presence of polar solvents favors the ionic structures, which may enhance the nitrogen hyperfine coupling constant. However, this explanation is not conclusive, and the problem of the solvent effect must be studied further.

The authors wish to thank Mr. Hideki Nakata for offering his data. The authors are also indebted to Dr. Kazuhiko Ishizu for his valuable discussions.