Electron Spin Resonance Hyperfine Spectra of Di-p-anisyl Nitric Oxide

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One of the present authors has previously reported the ESR study of diphenyl nitric oxide (DPNO) in the solid state[1] and in a liquid solution[2]. Similarly, the ESR study of di-*p*-anisyl nitric oxide, one of the derivatives of DPNO, has been reported by some authors[3-7]. Bijl and Rose-Innes[5], for instance, observed the ^{14}N hyperfine structure in a liquid solution for the first time. Roggen et al.[6] also observed the triplet hyperfine structure due to the ^{14}N nucleus; they interpreted it by assuming that the odd electron is associated mainly with the NO group. However, they did not find any evidence for the splitting or significant broadening of the lines by the proton moments. We have now observed the proton hyperfine spectra of di-*p*-anisyl nitric oxide in liquid solutions and have studied the effect of solvents on the spectra and on the width of nitrogen and proton hyperfine splittings.

Experimental

Following the method of Meyer et al.[8,9], we synthesized di-*p*-anisyl nitric oxide. This radical is very stable; it remains unchanged even six months after preparation. Solutions of di-*p*-anisyl nitric oxide were made in various kinds of solvent, i. e., benzene, toluene, cyclohexane, carbon tetrachloride, carbon disulfide, dimethoxyethane, tetrahydrofuran, acetone, acetonitrile, *n*-butyl alcohol, isopropyl alcohol, ethyl alcohol, methyl alcohol and water. These samples were contained in vacuum-sealed glass tubes. The solvents were completely dehydrated, degassed[2] and purified just before the preparation of the sample solutions. In order to determine the nitrogen and proton hyperfine coupling constants, an aqueous solution of peroxylamine disulfonate was used as a reference in the same manner as in the case of DPNO[2]. The ESR spectrometer employed was a JES-3B-type instrument of the Japan Electron Optics Co. This spectrometer is an X-band apparatus employing a cylindrical reflection cavity operated in the TE_{001} mode. The static magnetic field was generated by a JES electro-magnet with 300 mmϕ pole pieces, with a homogeneity of 10^{-6} gauss/sample volume. The magnetic field was modulated in 100 kilocycle/sec.

Results and Discussion

We observed the ESR spectra of di-*p*-anisyl nitric oxide in various kinds of solvent, thus determining a suitable concentration for obtaining a well-resolved hyperfine spectrum. In a properly diluted solution, a well-resolved hyperfine spectrum was obtained. Figure 1a* shows the ESR hyperfine spectrum of di-*p*-anisyl nitric oxide in the carbon tetrachloride solution. There are three large groups in the spectrum, and each of them splits further into many, about 160, fine absorption lines. These three groups arise from the interaction of the unpaired electron spin with the nuclear spin of ^{14}N, as has been suggested by Bijl and Rose-Innes[5] and by others[6,7], while the further splittings may be caused by the interaction with the proton moments. In Fig. 1a, the absorption lines show the effect of the anisotropy of molecular motion in solution, which results in a different line width for each line[10,11], as in the case of DPNO[2].

The measured *g*-value is 2.0054, and the ^{14}N hyperfine coupling constant is 10.20 gauss for the tetrahydrofuran (THF) solution. This coupling constant is a little larger than that of DPNO. This is perhaps because the electron-repelling effect of methoxy groups at the para position in the molecule of di-*p*-anisyl nitric oxide may enhance the unpaired-electron spin density at the nitrogen nucleus more than in the case of DPNO.

The structure of di-*p*-anisyl nitric oxide is shown in Fig. 1c. As the unpaired-electron spin density in this molecule has not yet been calculated, we can not compare the obtained spin density with the theoretically-calculated spin density. In order to explain the obtained

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* In all figures of the observed ESR spectra, the magnetic field was swept from the left hand side of a figure to the right.
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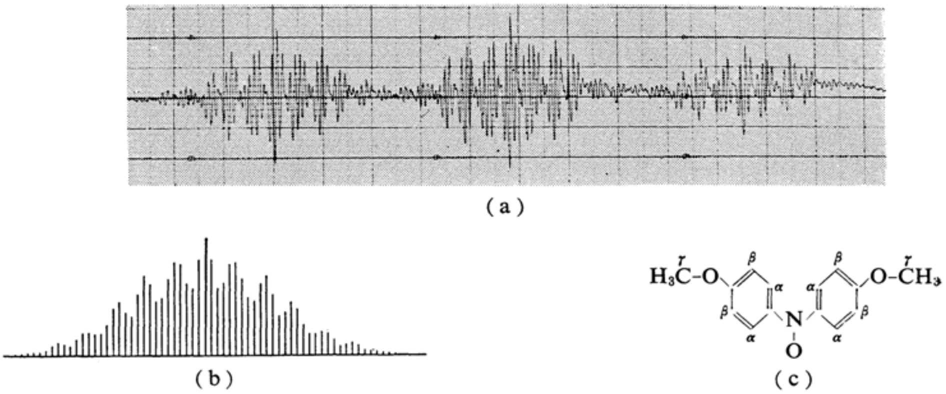
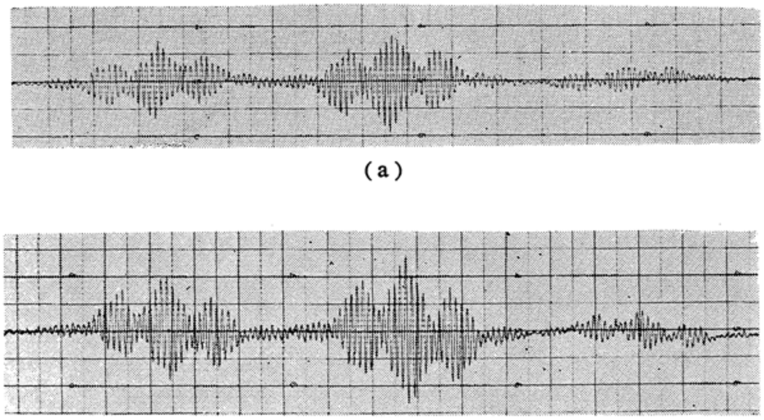


(a)

(b)

(c)

Fig. 1. (a) ESR spectrum of di-*p*-anisyl nitric oxide in CCl_4.
(b) Spectrum calculated based upon our assumption.
(c) The structure of di-*p*-anisyl nitric oxide.



(a)

(b)

Fig. 2. (a) The ESR spectrum of di-*p*-anisyl nitric oxide in *n*-butanol.
(b) The one in water solution.

ESR spectrum in Fig. 1a, however, one can assume that the ratios of the unpaired-electron spin densities at the α, β and γ positions of the molecule shown in Fig. 1c are 10 : 4 : 1 ; according to this assumption one can then construct such a spectrum as is shown in Fig. 1b. In this figure only one of the three groups is shown. Although, in Fig. 1a, the groups overlap with each other at the tails and although the outermost absorption lines are too weak to be distinguished from the noise level, it can be seen that the calculated spectrum in Fig. 1b shows a very good agreement with the observed ESR spectrum in Fig. 1a.

Spectra of a type similar to that obtained in the carbon tetrachloride solution were observed in relatively non-polar solvents, such as benzene, cyclohexane, dimethoxyethane and tetrahydrofuran. The resolution of the proton hyperfine splittings slightly changed from one solvent to another. However, in relatively strong polar solvents, such as acetone, acetonitrile, alcohols and water, a broadening of the line width is clearly observed and the number of proton hyperfine splittings decreases as compared with those in the cases of non-polar solvents. The spectra of the *n*-butanol solution and the aqueous solution are illustrated in Figs. 2a and 2b. In the case of alcohols and water, both of which have a hydroxyl group, the ESR spectra showed another remarkable change in that the absorption lines of the higher magnetic field group are strongly broadened compared with those of the lower one. This phenomenon can be considered to be a result of the strong anisotropic effect[2,11]; it may be illustrated qualitatively as follows. The alcoholic hydroxyl group has a very large affinity to the lone pair electrons of oxygen atoms in the molecule of di-*p*-anisyl nitric oxide, so that alcohol molecules will strongly solvate to the molecule of di-*p*-anisyl nitric oxide in solution.

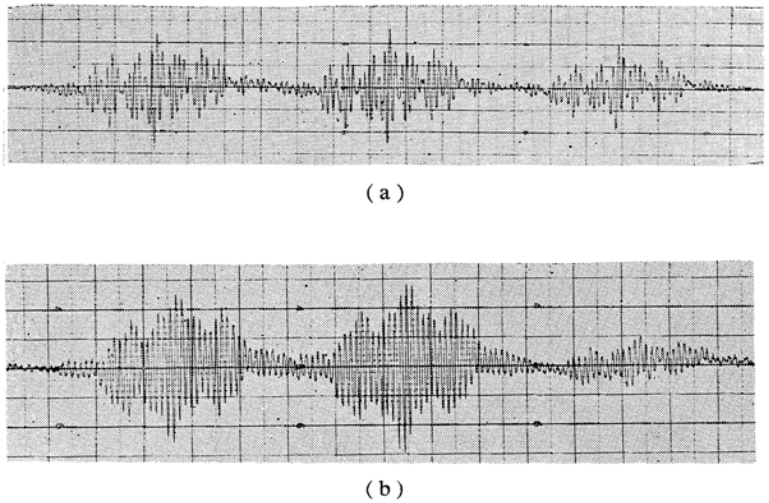


Fig. 3. (a) The ESR spectrum of di-*p*-anisyl nitric oxide in THF solution at room temperature 20°C.
(b) The one at −55°C.

Therefore, the motion of the solute radical will be reduced, and, consequently, the anisotropic effect will appear, causing a different set of relaxation times, T_2 and T_1, for each hyperfine line[2,10,11]. Thus we may explain this phenomenon, taking into account both the line-width calculation for DPNO[2], which revealed that the absorption lines of the higher magnetic field group were broader than those of the lower one, and the molecular similarity between DPNO and di-*p*-anisyl nitric oxide. For the quantitative varification of the above explanation, an experiment is expected to determine the *g*-tensor of di-*p*-anisyl nitric oxide.

To check the above explanation further, measurements were performed at low temperatures, since the viscosity of a solvent would increase at low temperatures. As an example, the ESR spectra of the THF solution are shown in Figs. 3a and 3b, where the former was measured at room temperature and the latter at −55°C. The latter spectrum is very similar to those shown in Fig. 2a and 2b. At a low temperature the free motion of the solute molecule is reduced and may be hindered as the viscosity of the solvent increases. The anisotropic effect, as a result, becomes appreciably large; it will broaden the width of each absorption line, especially those in the higher magnetic field group as compared with those in the lower magnetic field group, as is shown in Fig. 3b. This effect was not so remarkable in the case of DPNO. This is perhaps because DPNO has no methoxy group and because the free motion of the molecule of DPNO is not so strongly hindered by strong solvation or by the high viscosity of the solvent at a low temperature, as in the case of di-*p*-anisyl nitric oxide.

The effect of solvents on the widths of nitrogen and proton hyperfine splittings, which was first found in DPNO[2], was also found in di-*p*-anisyl nitric oxide. The results obtained are shown in Fig. 4 where the magnitudes of the dielectric constants of the solvents are conveniently taken as an abscissa scale. In this figure the alcoholic and aqueous solutions exhibit remarkably greater values than the others. This solvent effect will be explained qualitatively if one will consider

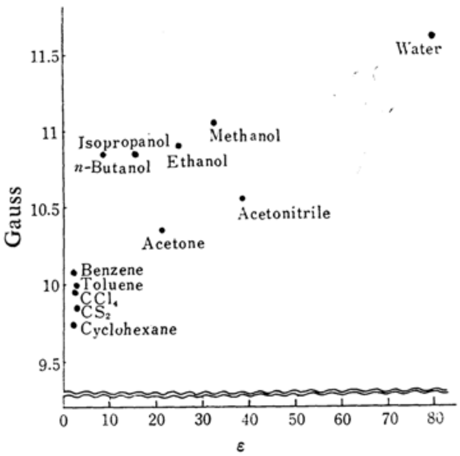


Fig. 4. Solvent effect on the nitrogen isotropic hyperfine coupling constant.

that the ionic structures of the radical molecule in the valence bond theory will be favored by the presence of polar solvents, as in the case of DPNO[2], so that the spin densities at the nitrogen and the ring carbons will be enhanced. Especially in the case of the alcoholic solution, these ionic structures may be much more favored by the effect of strong solvation. However, this explanation is not conclusive and further investigation is required to provide a rigorous theoretical basis.

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