

## ESR Spectra of Some Phenyl Nitroxide Radicals

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**Abstract** : Phenyl nitroxide radicals were obtained by UV irradiation on phenyl hydroxylamine-dioxane solutions containing oxygen gas. ESR parameters determined from analysis of these spectra were very close with the only exception in the case of methyl proton hyperfine splitting  $A_{H(CH_3)}$  in all tolyl nitroxide radicals. Hyperfine splitting of methyl proton *o*-, *m*-, and *p*-tolyl nitroxide radicals were 1.98, 0.97, and 3.02 G respectively. Such nonconstancy between the hyperfine splitting of methyl proton in *o*- and *p*-tolyl nitroxide radicals is an very interesting result and it may be explained by the steric interactions between NO group including unpaired electron and methyl group out of phenyl plane.

### Introduction

Many ESR studies on phenyl nitroxide radicals have been reported<sup>1,2)</sup>. In these papers, they ascertained the constancy of the ratio of hyperfine splitting of nitrogen to that of hydrogen attached to nitrogen in phenyl nitroxide radicals produced by methods using various oxidants. Nishikawa and Someno<sup>2)</sup> have especially concluded that all the effects of solvents, substituents and steric hinderance give only less than 1% change on the ratio of hyperfine splitting of nitrogen to that of hydrogen attached to it,  $A_N/A_{H(N-H)}$ . The results seem to imply all phenyl nitroxide radicals being coplanar structure but they didn't discuss on the effect of substituents on the hyperfine splitting of substituent themselves and the radical structure.

Present author followed the effect of substituents on hyperfine splitting of substituents in phenyl nitroxide radicals produced by UV irradiation using chloro atom as typical electron-withdrawing substituent and methyl group as electron-donating substituent, and found an existence of steric interactions affected on the hyperfine splitting of methyl proton in *o*- and *m*- tolyl nitroxide radicals. The interaction may be the nonplanar steric interactions between the methyl group and NO group containing unpaired electron, resulting the reduce in hyperfine splitting of methyl proton in tolyl nitroxide radicals.

### Experimental

Phenyl hydroxylamine, tolyl hydroxylamines, and chloro benzene hydroxylamines were prepared by reduction of corresponding nitro benzene, nitro toluenes and chloro nitrobenzenes with zinc powder and ammonium chloride,<sup>3)</sup> and stored in freezer under nitrogen gas atmosphere. Samples were prepared by passage of oxygen gas through phenyl hydroxylamine-dioxane solutions in ESR sample tube (4 mm Supura) and followed by UV irradiation without UV filter at room temperature. JEOL ES-UV 05 X (Wacom Xenon lamp 500 W) was used as UV light source. ESR spectra were recorded at room temperature after

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degassing.

### Results and discussion

When dioxane solutions of phenyl hydroxylamine derivatives were UV irradiated, ESR spectra expected from corresponding nitroxide radicals were obtained. Typical ESR spectra of phenyl nitroxide and *o*- and *p*-tolyl nitroxide radicals are shown in Fig. 1 (a), (b), and

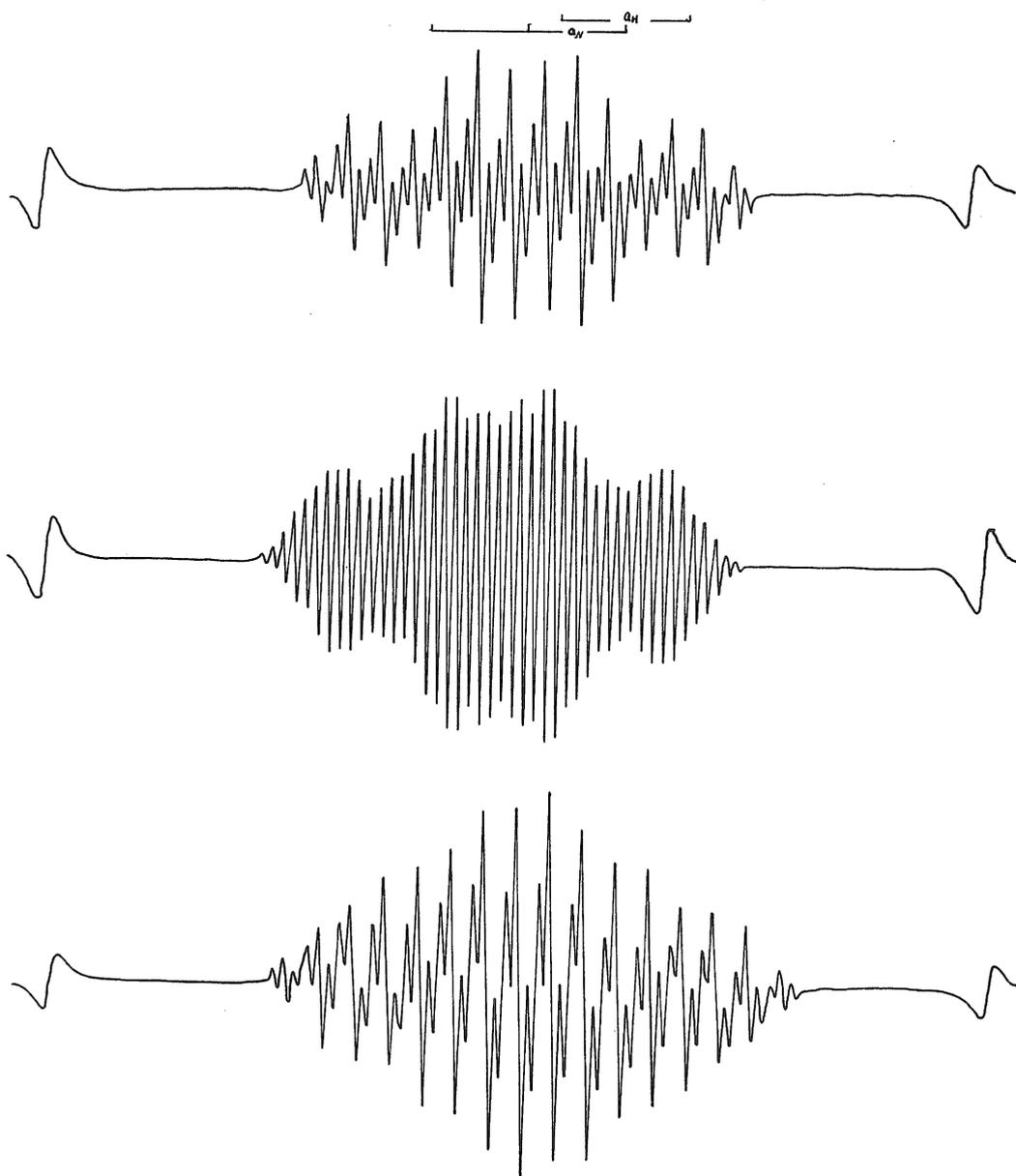


Fig. 1 ESR Spectra of (a) phenyl nitroxide radical, (b) *o*-tolyl nitroxide radical, and (c) *p*-tolyl nitroxide radical produced by UV irradiation on dioxane solutions of phenyl hydroxylamine, *o*-tolyl hydroxylamine, and *p*-tolyl hydroxylamine, respectively.

Phenyl nitroxide radicals	g values	Hyperfine coupling constants (G)					Ratio $a_N/a_{H(N-H)}$
		$a_N$	$a_{H(N-H)}$	$a_H^{o,p}$	$a_H^m$	$a_H^{CH_3}$	
phenyl nitroxide	2.0057	9.13	12.12	2.98	0.97		0.753
		9.58	12.67	3.02	0.98 <sup>2)</sup>		0.756
<i>o</i> -tolyl nitroxide	2.0057	9.06	12.07	3.01	0.99	1.98	0.751
<i>m</i> -tolyl nitroxide	2.0057	9.05	12.07	3.02	0.96	0.96	0.750
<i>p</i> -tolyl nitroxide	2.0057	9.18	12.21	3.06	0.97	3.02	0.752
		9.44	12.47	3.10	1.12	3.10 <sup>2)</sup>	0.757
<i>o</i> -chlorobenzene nitroxide	2.0059	8.68	11.77	3.14	1.04		0.737
<i>m</i> -chlorobenzene nitroxide	2.0057	8.88	11.85	2.98	1.01		0.749
<i>p</i> -chlorobenzene nitroxide	2.0060	8.88	11.87	3.00			0.748

TABLE 1. ESR Parameters from phenyl nitroxide radicals produced by UV irradiation.

(c), respectively, in which hyperfine splitting of nitrogen, phenyl proton, and methyl proton can be observed. ESR parameters determined from analysis of these spectra are very similar with those in literatures<sup>1,2)</sup>, and are listed in Table 1. As can be seen from Table 1, hyperfine splitting of nitrogen and hydrogen attached to it in all tolyl nitroxide radicals are slightly larger than those in all chloro benzene nitroxide radicals, nevertheless the ratio of hyperfine splitting of nitrogen and hydrogen attached to it,  $A_N/A_{H(N-H)}$ , are almost the same. The results seem to reflect the tendency of electronegativity between the methyl group and chloro atom as substituent group. Namely, introduction of chloro atom as electron-withdrawing substituent into the phenyl ring may result in larger reduction in the magnitude of the  $A_N$  and  $A_H$  values. On the contrary, the introduction of methyl group as electron-donating substituent may lead to a little decrease in the magnitude of  $A_N$  and  $A_H$  values.

A very interesting result is furthermore involved in Table 1. In tolyl nitroxide radicals, hyperfine splitting of methyl proton in *o*-, *m*-, and *p*- position are 1.98, 0.96, and 3.02 G respectively. It is reasonable that hyperfine splitting of *m*-methyl proton is the smallest from the resonance in phenyl ring. However, it is very difficult to appreciate that hyperfine splitting of *p*-methyl proton is 1.5 times larger than that of *o*-methyl proton in spite of the same hyperfine splitting of *o*-, and *p*-phenyl proton in tolyl nitroxide radicals. Such abnormality of methyl proton splitting in tolyl nitroxide have not been reported.

The abnormality of phenyl proton in iminoxy benzoquinone radicals was however reported by Gilbert *et al.*,<sup>4)</sup> who the largest proton splitting in rigid iminoxy radicals to hydrogen spatially close to the oxygen of the iminoxy group. Steiberger and Fraenkel<sup>5)</sup> have observed the five different ring proton splitting in acetophenone and benzaldehyde anion radicals. Thus the abnormality in hyperfine splitting of ring proton were explained by the interaction between NO group or substituent and ring proton. In this work, abnormality of hyperfine splitting is found in not ring proton but methyl proton and so it may be explained by the interaction between NO group and methyl group. It may be supported by the fact *o*-tolyl hydroxylamine is oil because strong intermolecular interaction is involved, while *p*-tolyl hydroxylamine is solid for weak intermolecular interaction. Also the fact

lifetime in *o*-tolyl nitroxide radical being shorter than that in *p*-tolyl one imply that *o*-tolyl nitroxide radical could not have a stable coplanar structure on account of steric interaction between NO group and methyl group. Methyl group in *o*-position may interact with NO group out of phenyl plane, and seems not to effect the hyperfine splitting of proton in *o*- and *p*-position. Methyl group in *p*-position weakly interact with NO group and so doesn't effect on the hyperfine splitting of proton in *o*-position.

It is also hard to understand that spin density of methyl proton in *m*-position is the same as that of phenyl proton in *m*-position in *m*-tolyl nitroxide radical. The fact may be also explained by the steric interaction between methyl group and NO group out of phenyl plane. Thus hyperfine splitting of methyl proton is expected to reduce less than that of phenyl proton by the steric interaction and so the spin density of methyl proton in *m*-position may take negative value. Further detail discussions and molecular orbital calculations on the steric interactions between substituent and NO group containing unpaired electron will be reported in future along with similar abnormality found in 2, 6 dimethyl and 2, 4 dimethyl nitroxide radicals.

### References

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