Secondary Spin Adducts Derived from Aryl Radicals and 2-Methyl-2-nitrosopropane. Radical Chromato-ESR Spectroscopy and Numerical Decoupling Analysis Studies

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Spin adducts obtained from 2-methyl-2-nitrosopropane (MNP) and phenyl or *para*-substituted phenyl radicals have been studied by means of radical chromato-ESR spectroscopy. Several previously unknown spin adducts have been isolated and detected in addition to the primary spin adducts of aryl-t-butylaminoxyl radicals. The newly obtained spin adducts have been found to be secondary spin adducts which result from the reaction of the primary spin adducts with aryl radicals. The structures of some of the secondary spin adducts have been shown to be *o*-(aryl)aryl-t-butylaminoxyl radicals, a variety of sterically hindered aminoxyl radical. This type of aminoxyl radical has been studied for the first time in this work. The hyperfine coupling constants of the spin adducts have been determined using NMR spectroscopy and a numerical decoupling analysis (NDA). The spin density at the *meta*-protons in these radicals was unusually high. This can be ascribed to the largely steric hindrance between the t-butyl and the *ortho*-phenyl groups. The formation pathways of these secondary spin adducts have also been revealed.

It has been recognized that free radicals play an important role as intermediates in various chemical reactions. A spin trapping technique [1] is one of the simplest methods by which a short-lived free radical can be detected and its structure studied. With this technique, an unstable free radical reacts with a nitroso or nitrone compound and is converted into a stable aminoxyl radical called a spin adduct, the ESR spectrum of which provides us with detailed information on the structure of the unstable free radical.

However, when many free radicals are formed and trapped simultaneously, it is difficult to elucidate each spin adduct in an overlapped ESR spectrum. Spin trap-radical chromato-ESR (ST-RC-ESR) spectroscopy [2] has been developed recently by the author (H. H.) as one of the means of overcoming this problem and has been applied to the analysis of short-lived radicals produced not only in the γ-irradiated aqueous systems of several nucleotides, amino acids and peptides [3a] but also to ultrasonic irradiated [3b] and photochemical systems.[3c,d] In these studies, 2-methyl-2-nitrosopropane (MNP) has been used as a spin-trapping reagent because the ESR spectrum of the resulting spin adduct contains much information on the structure of the trapped radical.[4]

In the present work, we studied the structures and the formation mechanisms of the secondary spin adduct detected in aryl radical and MNP systems in acetonitrile. Aryl radicals were produced by the reduction of aryldiazonium salts with iodide as follows:

$$Ar{-}N{\equiv}N^{+} + e^{-} \longrightarrow Ar{-}N{=}N^{\bullet} \longrightarrow Ar^{\bullet} + N_2$$

In the reduction of of benzenediazonium salts and their derivatives, the corresponding aryl radicals were detected using the spin trapping technique with MNP [6a] or with α-phenyl-t-butylnitrone (PBN).[6b]

However, additional spin adducts could be separated by using the ST-RC-ESR method. Though it suggested that other radicals were also involved in the systems, the radicals obtained were eventually found to be the secondary spin adducts which were generated from the reaction of the primary spin adducts with aryl radicals. These results were quite unexpected to us because the MNP and aryl radical systems have been already examined by many workers,[7a,b] nevertheless there have been no reports on such secondary spin adducts.

Since the ESR spectra of these secondary spin adducts were poorly resolved and complex, we have developed a numerical decoupling analysis (NDA) for the analysis of low-resolution ESR spectra.[8] NDA is a computer-assisted method for the high resolution analysis of isotropic ESR spectra. In this analysis, hyperfine coupling constants (hfccs) for nuclei with $I = 1/2$ involved in the ESR spectra observed can be accurately determined from the positions of the peaks which appear in an $I_2(x)$ plot. (The subscript indicates the multiplicity of the nuclear spin of $I = 1/2$, namely, $2I + 1 = 2$.)

By using NDA together with the observation of Knight shifts, the secondary spin adducts were determined to be *o*-(aryl)aryl-t-butylaminoxyl radicals, which have not so far been studied, in spite of the long history of aminoxyl radicals.[9]

Results and Discussion

(*a*) *Spin Adducts Obtained in the MNP and* para-*Substituted Phenyl Radical Systems.*—Figure 1(*a*) shows the ESR spectrum of the spin adducts which were obtained when *p*-nitrobenzenediazonium salt was reduced with iodide ion in the presence of MNP. The spectrum shows that several spin adducts with different nitrogen hfccs due to the N–O group (a_N) are mixed. Figures 1(*b*) and 1(*c*) show spin adducts which could be detected by the ST-RC-ESR technique. It should be pointed out that the ESR spectrum in Figure 1(*c*) shows a distinct hyperfine structure which was completely concealed before separation. An inspection of the ESR spectrum in Figure 1(*b*) revealed that the structure of the spin adduct was radical (**1a**) and thus the trapped radical was assumed to be the *p*-nitrophenyl radical.

Similar results were obtained with *p*-cyano- and *p*-chlorophenyl radicals. In each case, two different spin adducts were detected. One of them was found to be *p*-cyano- or *p*-chlorophenyl-t-butylaminoxyl, respectively. These spin-adduct hfccs are summarized in Table 1. On the other hand, the ESR spectra of the other spin adducts were poorly resolved, as shown in Figure 1(*c*). The interpretation of these spectra was quite

Table 1. Hfccs/mT of *para*-R substituted phenyl-t-butylaminoxyl radicals obtained as spin adducts produced in the MNP and *para*-R substituted phenyl radical system (in benzene).

R	Structure	a_N	$a_H(o)$	$a_H(m)$	$a_R(p)$
NO_2	(**1a**)	1.06	0.233	0.088	0.0555 (1 N)
CN	(**1b**)	1.09	0.2215	0.0905	0.032 (1 N)
Cl	(**1c**)	1.21	0.205	0.089	—
H	(**1d**)	1.23	0.180	0.082	0.180 (1 H)

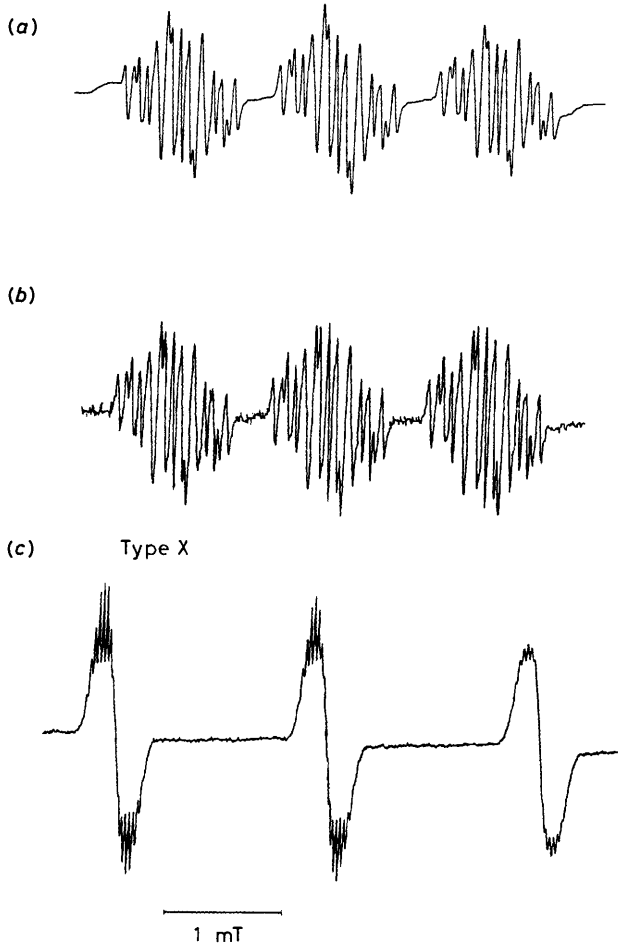
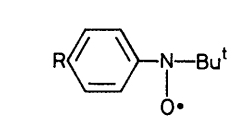
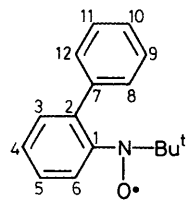


Figure 1. ESR spectra of spin adducts produced in the reduction of *p*-nitrobenzenediazonium salt in the presence of MNP: (*a*) before separation; (*b*) eluted initially from a silica gel column; and (*c*) second eluted fraction.

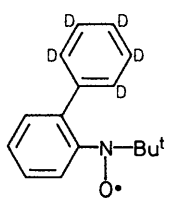


(**1**)

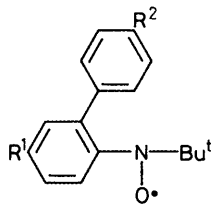
a; R = NO_2
b; R = CN
c; R = Cl
d; R = H



(**2**)



(**3**)



(**4**)

a; $R^1 = R^2$ = Cl
b; $R^1 = R^2$ = CN
c; R^1 = H, $R^2 = NO_2$
d; $R^1 = R^2 = NO_2$

difficult simply by conventional analysis. Hereafter, we call the latter spin adducts Type X.

We attempted to observe electron–nuclear double resonance (ENDOR) spectra in order to determine the hfccs of the Type X spin adducts. However, no meaningful spectra could be obtained. This is probably because the ENDOR signals of this type of radical were difficult to observe, and moreover only small amounts of these spin adducts could be obtained in all cases.

(*b*) *Spin Adducts Obtained in the MNP and Phenyl Radical System.*— In this system, three spin adducts could be separated and detected by chromatography (Figure 2). Two were readily proved to be diphenylaminoxyl[10] [Figure 2(*a*)] and t-butylphenylaminoxyl radicals[11] [Figure 2(*b*)].

The ESR spectrum of the third adduct [Figure 2(*c*)] was similar to that in Figure 1(*c*), namely, there are three well-separated parts and each part gives a poorly resolved hyperfine structure [Figure 3(*c*)]. Therefore, the third spectrum corresponds to the Type X spin adducts. The a_N value of this spin adduct was as great as 1.48 mT, which indicates that the unpaired electron is localized on the N–O group. In addition, the ESR spectrum of the third spin adduct obtained for the [$^2H_5$]phenyl radical can be simulated with only nine t-butyl protons at 0.0285 mT [Figures 3(*b*) and 3(*c*)]. These features are similar to those of *ortho*-subsituted phenyl-t-butylaminoxyls (which are sterically hindered aminoxyl radicals).[12–14]

In a sterically hindered radical, the N–O group cannot be in the same plane as the phenyl ring due to the steric interaction between the *ortho*-substituent and the N–O and t-butyl groups, and overlapping of the p-orbital in the N–O group and the π orbital on the phenyl ring is therefore small. As a result, the hfccs of the ring protons become fairly small and the order has been observed to be $a_H(o) > a_H(m) >> a_H(p)$ which is quite different from the order $a_H(o)$, $a_H(p) \approx 2a_H(m)$ which is observed in the unhindered one.[14] In contrast, because the unpaired electron is localized on the N–O group, the a_N value and the hfcc of the t-butyl protons [$a_H(Bu^t)$] become great, and values of *ca.* 1.2–1.5[12] and 0.02–0.03 mT, respectively, are usually observed.

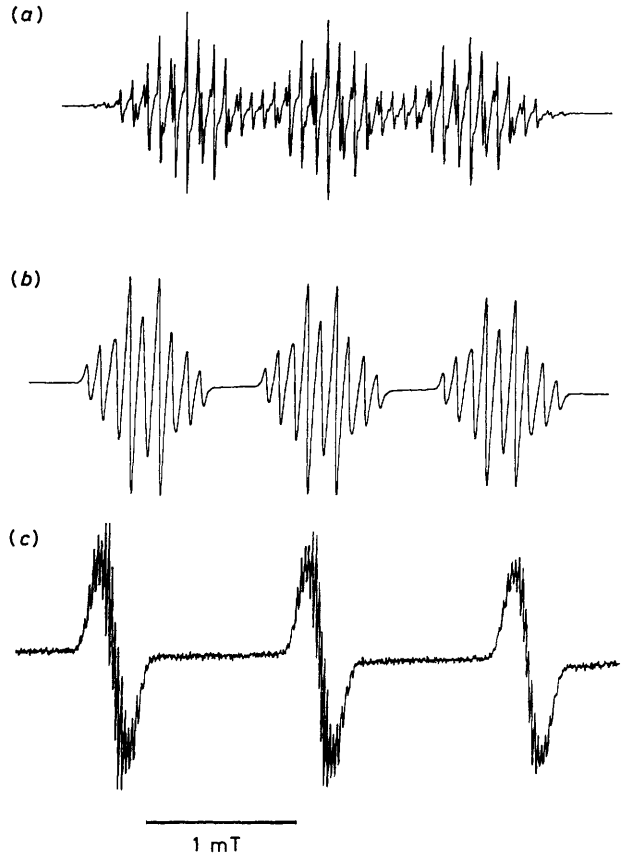


Figure 2. ESR spectra of spin adducts detected in the system of phenyl radical and MNP; (*a*) first fraction eluted from a silica gel column; (*b*) second fraction; and (*c*) third fraction.

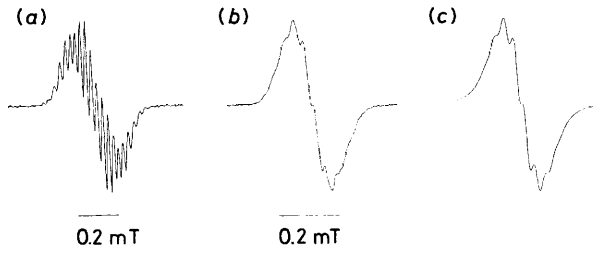


Figure 3. (*a*) Expanded ESR spectrum of the $M_I = +1$ components of Type X spin adduct which was obtained in the phenyl radical and MNP system. (*b*) Same as (*a*) but for the perdeuteriophenyl radical. (*c*) Simulated ESR spectrum at 0.0285 mT (9 H).

These values are characteristic of hindered radicals since a_N is observed to be *ca.* 1.1–1.4 mT,[11] and $a_H(Bu^t)$ contributes only to the line-broadening for unhindered radicals.[14]

Considering these results and the possibility of arylation of the t-butylphenylaminoxyl radical, we presumed that the third spin adduct was radical (**2**). This prediction could be readily verified by comparing the ESR spectrum in Figure 3(*a*) with that of radical (**2**) synthesized as described later.

Next, the Knight shift in the NMR spectrum of radical (**2**) was observed in order to assign exactly the hfccs. The amount of Knight shift for a proton is represented by equation (1)[15]

$$\Delta H/H = -7.30 \times 10^{-4} a_H \quad \text{at 303 K} \qquad (1)$$

where $\Delta H/H$ is the relative shift to its position in an equivalent diamagnetic compound, and a_H is the hfcc of the proton in mT.

Figure 4(*a*) shows the ^{1}H NMR spectrum of a solution (*ca.* 1 mol dm^{-3}) of radical (**2**) in [$^2H_6$]benzene. Furthermore, the ^{1}H NMR spectrum of radical (**3**) [Figure 4(*b*)] was observed to distinguish the hfccs of the ring protons from those of the *o*-phenyl group. Assignments of the hfccs are summarized in Table 2. $a_H(p)$ in the *o*-phenyl group was not determined because the NMR peak overlapped with that of C_6D_5H, indicating that the hfcc is fairly small.

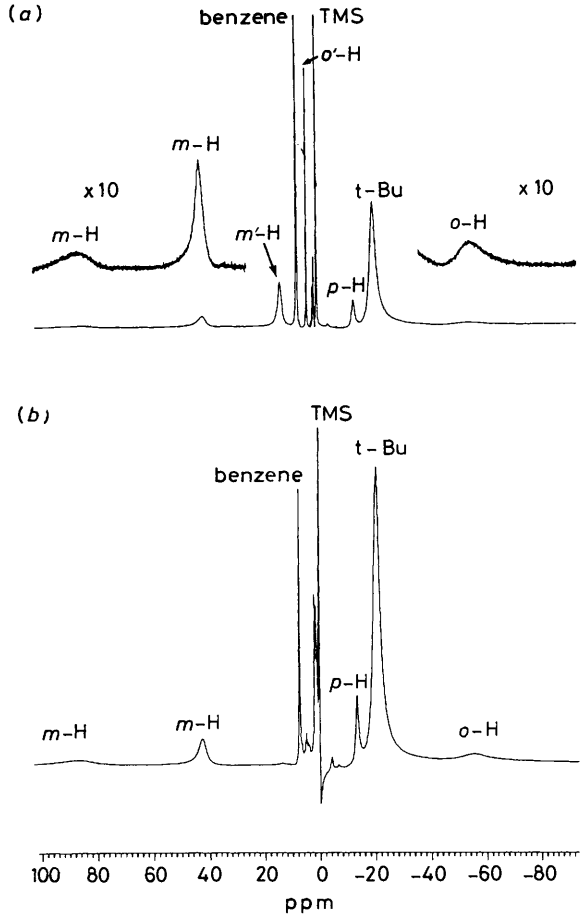


Figure 4. ^{1}H NMR spectra of a [$^2H_6$]benzene solution of (*a*) radical (**2**) and (*b*) radical (**3**) at 303 K. The distortion appearing in the TMS signal is probably due to a slight maladjustment of the phase angle.

We considered it strange that two $a_H(m)$ values are quite different and that one of them is larger than $a_H(o)$ for radical (**2**). It can be expected that the unpaired electron penetrates to the ring protons mainly through the σ bond in steric hindred aminoxyl radicals, and thus $a_H(o)$ should be greater than $a_H(m)$. This is true for many of these hindered aminoxyl radicals except for *o*-chloro and *o*-bromo compounds for which $a_H(m)$ is slightly greater than $a_H(o)$.[12]

For a further investigation of this reversal, the hfccs of the ring protons were calculated using the INDO method.[16] However, in spite of calculations involving various dihedral angles between the C(Ar)–N–O and phenyl planes, an order similar to that observed could not be obtained with any angles.

The a_N value of radical (**2**) is the greatest of those reported for *ortho*-substituted phenyl-t-butylaminoxyl radicals.[12–14] This suggests that the phenyl ring twists more than for other sterically hindered cases. Therefore, the failure of the MO calculations is probably attributable to some conformation distortions in the molecule arising from the interaction between the *o*-phenyl and t-butyl groups.

(*c*) *Elucidation of Type* X *Spin Adducts by means of* NDA.—Figure 5(*a*) shows the ESR spectrum of the Type X spin adduct

Table 2. Hfccs/mT of the Type X spin adducts (in benzene).

R	Structure	a_N	$a_H(Bu^t)$	$a_H(o)$	$a_H(m_1)$	$a_H(m_2)$	$a_H(p)$	a_H(*o*-Ph)
H	(**2**)	1.48	0.0285	0.0740	0.1020	0.0485	0.0285	0.007[a] (2 H)
	(**3**)	1.48	0.0285	0.0750	0.1035	0.0485	0.0285	—
	(**2**)		−0.0280	−0.0821	+0.1041	+0.0458	−0.0284	−0.0051 (2 H, *o*) +0.0079 (2 H, *m*)[b] 0 (1 H, *p*)
Cl	(**4a**)	1.45	0.0265	0.0730	0.1010	0.0475	—	0.007[a] (2 H)
CN	(**4b**)	1.43	0.0260	0.0845	0.0965	0.0500	*ca.* 0 (1 N)	0.005[a] (2 H)
NO_2	(**4d**)	1.41	0.0240	0.0820	0.0930	0.0450	0.013 (1 N)[a]	0.005[a] (2 H)

[a] Estimated value using ESR simulation. [b] Calculated from the ^1H NMR spectrum observed in a [$^2H_6$]benzene solution (*ca.* 1 mol dm^{-3}) at 303 K.

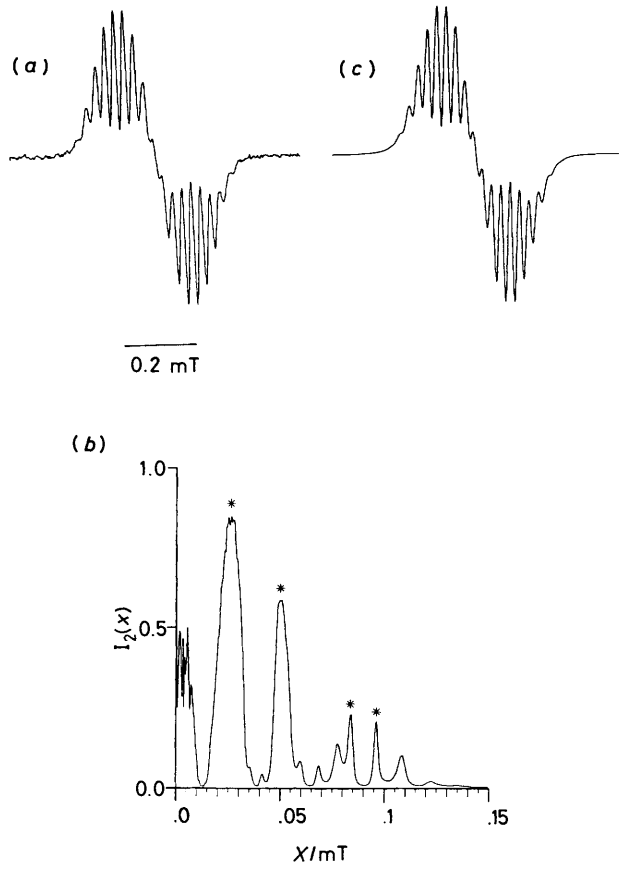


Figure 5. (*a*) Expanded ESR spectrum of the $M_I = +1$ components of Type X spin adduct for the *p*-cyanophenyl radical. (*b*) $I_2(x)$ plot for spectrum (*a*). Asterisks denote proton hfccs. (*c*) Simulated ESR spectrum using the parameters listed in Table 2.

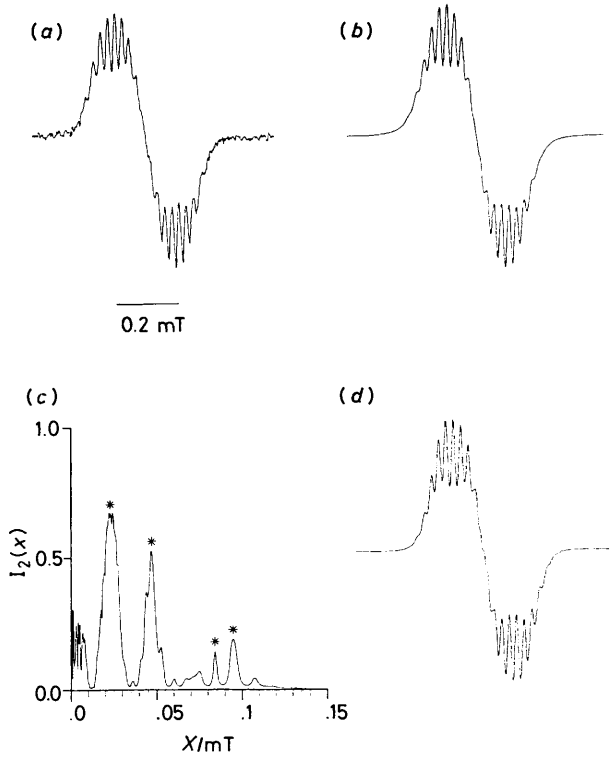
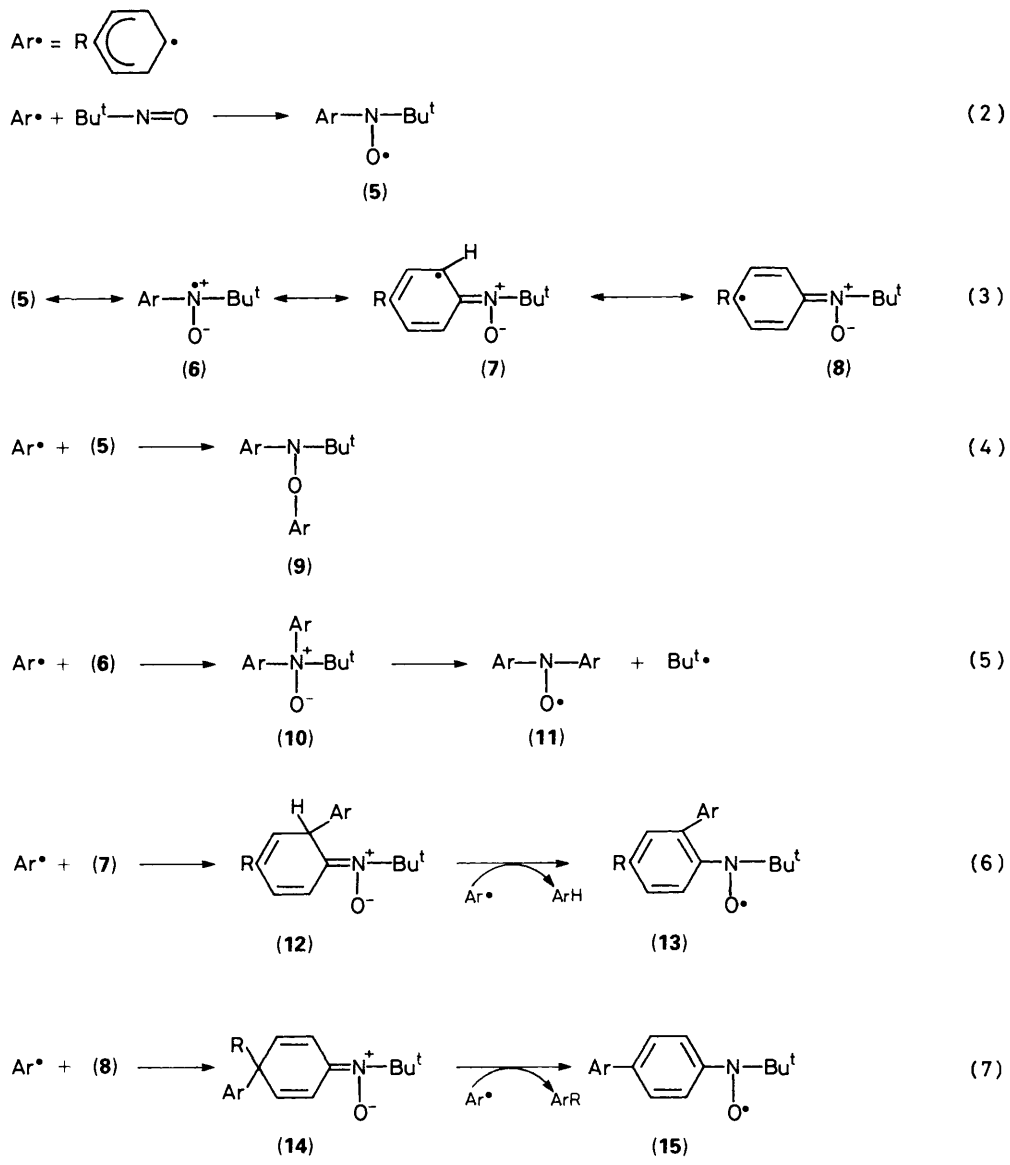


Figure 6. (*a*) Expanded ESR spectrum of the $M_I = +1$ components of Type X spin adduct for *p*-nitrophenyl radical. (*b*) $I_2(x)$ plot for spectrum (*a*). Asterisks denote proton hfccs. (*c*) ESR spectrum simulated at 0.024 (10 H), 0.045 (1 H), 0.082 (1 H), and 0.093 mT (1 H), and (*d*) the spectrum at 0.024 (9 H), 0.045 (1 H), 0.082 (1 H), 0.093 (1 H), 0.013 (1 N), and 0.005 mT (2 H).

for the *p*-cyanophenyl radical. From the peak positions marked with asterisks in the $I_2(x)$ plot [Figure 5(*b*)], four proton hfccs, 0.026, 0.050, 0.0845, and 0.0965 mT, could be obtained. The numbers of equivalent nuclei for each hfcc were easily determined with digital simulation; nine for 0.026 mT, one for the other hfccs. The ESR spectrum simulated with these parameters and small proton hfccs, 0.005 mT (2 H, *o*-phenyl), was in good agreement with the observed one [Figure 5(*c*)]. Thus, it was proved that the structure of the spin adduct is radical (**4b**).

Interpretation of the ESR spectrum in Figure 1(*c*) was rather difficult. Though the $I_2(x)$ plot shown in Figure 6(*b*) was similar to that of the *p*-cyano compound [Figure 5(*b*)], the simulated spectrum [Figure 6(*c*)] with hfcc values 0.024 [$a_H(Bu^t)$], 0.045 [$a_H(m)$], 0.082 [$a_H(o)$], 0.093 [$a_H(m)$], and 0.024 mT [$a_H(p)$] was in good agreement with the observed one. However, the simulated spectrum with hfccs 0.024 [$a_H(Bu^t)$], 0.045 [$a_H(m)$], 0.082 [$a_H(o)$], 0.093 [$a_H(m)$], and with hfccs smaller than the line width, 0.005 mT (a_H, 2 H) for ring protons in the *o*-phenyl group and 0.013 mT [$a_H(NO_2)$] for the *p*-nitro group was also the same as that observed [Figure 6(*d*)]. The parameters sets for the former and the latter correspond to the structures of radicals (**4c, d**), respectively. While the structure of radical (**4d**) is similar to the other *para*-substituted radicals, the *p*-nitro group is replaced by a hydrogen atom in the case of radical (**4c**).

Though it is impossible to confirm the exact structure of the spin adduct from the results of the simulation, radical (**4d**) is thought to be reasonable for the following reasons. First, there is a similarity between the ESR spectrum in Figure 6(*a*) and that of radical (**4b**) [Figure 5(*a*)]. The Hammett value for the cyano group ($\sigma p = 0.66$) is close to that for the nitro group ($\sigma p = 0.78$) and hence the similarity between the ESR spectra is very close provided the structure does in fact belong to radical (**4d**).



Scheme.

The fact that the proton hfccs for radicals (**1a**, **b**) are almost the same (Table 1) also supports this prediction. Second, if the structure belongs to radical (**4c**), its ESR spectrum is probably similar to that of radical (**2**) [Figure 3(*a*)] because very small effects due to the *p*-nitro group in the *o*-phenyl group can be expected on the spin densities in the ring protons. However, the pattern of hyperfine structure for the former was quite different from that for the latter. Thus, we concluded that the spin adduct must be radical (**4d**).

The hfccs determined with NDA are summarized in Table 2. It is difficult to assign the hfccs to the *o*- and *m*-protons simply by analysing the ESR spectra. We assumed that the hfccs of the ring protons were not greatly changed, and hence that the relation $a_H(m_1) > a_H(o) > a_H(m_2)$ holds for these radicals because the degree of steric effects is presumed to be almost independent of the *para*-substituents.

The hfccs of radicals (**2**) and (**3**) are slightly different from those obtained by NMR spectroscopic studies though the ESR simulations using these hfccs were in good agreement with the observed ones. This reason can probably be attributed to the large difference in the concentration of radicals between the NMR (> 1 mol dm^{-3}) and the ESR spectral observations (< 0.1 mmol dm^{-3}).[13]

(*d*) *Formation Pathways of Type* X *Spin Adducts.*—As described previously, the reaction of aryl radicals with aryl-t-butylaminoxyl radicals is the most probable formation pathway of Type X spin adducts. To verify this prediction, we reduced benzenediazonium salt in the presence of a large amount of the synthesized t-butylphenylaminoxyl radical instead of MNP. After the reaction had reached completion, radicals (**2**) and diphenylaminoxyl radicals could be detected. These results indicate that another aminoxyl radical (secondary spin adduct) is produced from the reaction of an arylaminoxyl radical (primary spin adduct) with aryl radicals. The formation pathway for these spin adducts is believed to be as shown in the Scheme.

A series of limiting structures expressed by equation (3) is well known.[17] The intermediates (**9**), (**10**), (**12**), and (**14**) are expected to be produced from the reaction of aryl radical with the limiting structures (**5**)–(**8**), respectively. Aminoxyl radicals combine readily with free radicals to give the *O*-substituted hydroxylamine according to equation (4). This coupling process has been

proposed by Wieland *et al.*[18] Diphenylaminoxyl radical (**11**) may be produced from intermediate (**10**) after release of the t-butyl group [equation (5)]. Radical (**13**), corresponding to Type X spin adduct can be formed if the proton in intermediate (**12**) is abstracted by another aryl radical [equation (6)]. Though in the same way, radical (**15**) is expected to be formed when X = H [equation (7)], this radical was not detected. Although the diarylaminoxyl radical produced in the replacement reaction [equation (5)] should be detected in the case of the *para*-substituted phenyl radical, this radical was not detected either. It is probably because it is formed in only small amounts and is less stable than radical (**13**).

On the other hand, no secondary spin adducts were detected from the *ortho*-substituted phenyl radicals. The reasons are as follows; the spin density at the *o*- or *p*-protons is fairly small in sterically hindered aminoxyl radicals.[14] This means that the limiting structures (**7**) and (**8**) contribute less to their properties and therefore the reaction with aryl radicals hardly occurs. Moreover, these radicals may hardly be attacked at the nitrogen atom due to steric hindrance. These propositions are supported by the facts that sterically hindered radicals are usually stable.[19]

The reactions of indolinone aminoxyl radicals with aminyl or aroyloxyl radicals have been reported to give the ring-substituted radicals.[20] However, neither the replacement reaction [equation (5)] nor the arylation of arylaminoxyl radical [equations (6) and (7)] have been studied.

Forrester reported that arylamimoxyl radicals decompose by the coupling of the aminoxyl oxygen atom to the *para*[21] or *ortho*[22] position of another molecule. This strongly supports the existence of the coupling reaction of a reactive radical to the *para* or *ortho* position of the arylaminoxyl radical [equations (6) and (7)].

It is important to point out that the secondary spin adducts can be produced by the reaction of spin adducts with unstable radicals. In fact the spin adduct assigned as radical (**5**) did not result from the capture of *o*-biphenylyl radical by MNP but was a secondary spin adduct. It is impossible to determine whether the spin adduct is primary or secondary simply from an analysis of the ESR spectrum. The formation of secondary spin adducts must therefore be considered in any spin-trapping technique, especially in mechanistic studies of radical reactions.

Judging from the above formation mechanisms, such secondary spin adducts may be detected when an unhindered arylaminoxyl radical is produced as the primary spin adduct; *e.g.* when free radicals are trapped with nitrosobenzene or when aryl radicals are trapped with a nitroso compound. Furthermore, since secondary spin adducts result from the reaction of the primary spin adduct with aryl radicals, they may readily be formed when a large amount of free radicals is involved in the reaction system.

Conclusions

In the MNP and *para*-substituted phenyl radical systems, secondary spin adducts could be successfully separated and detected by the ST-RC-ESR technique. Two secondary spin adducts could be obtained in addition to the primary spin adduct, especially in the case of phenyl radical. One of them was easily found to be diphenylaminoxyl radicals. From a thorough investigation by NMR spectroscopy and NDA, the remaining secondary spin adducts were determined to be *o*-(aryl)aryl-t-butylaminoxyl radicals. The spin densities at the *meta*-protons in these radicals were quite unusual due to the largely steric hindrance between the t-butyl and the *o*-phenyl groups.

The formation pathways of these secondary spin adducts were revealed as follows; diphenylaminoxyl radical was formed from the replacement reaction by phenyl radical, and *o*-(aryl)aryl-t-butylaminoxyl radicals were produced from the arylation of aryl-t-butylaminoxyl radicals.

Experimental

(*a*) *Preparations of Materials.*—(i) *Spin trapping reagents and general reagents.* 2-Methyl-2-nitrosopropane (MNP) was synthesized and purified according to the method of Stowell.[23] t-Butylphenylaminoxyl radicals were synthesized by standard methods.[24] [$^2H_6$]Benzene (99.5 atom % D), [$^2H_5$]aniline (99 atom % D) were purchased from the Aldrich Chemical Company, and *o*-bromobiphenyl was obtained from Tokyo Kasei Co., Ltd. Silica gel (Wakogel C-200) was from Wakenyaku Co., Ltd. All other chemicals were of reagent grade.

(ii) *Preparation of aryldiazonium tetrafluoroborates.* An aqueous solution of aryl diazonium chloride was prepared by a method similar to that reported by Bullard and Dickey.[25] After the addition of an excess of sodium tetrafluoroborate to this solution, the resulting precipitate was filtered, washed with acetone and dried over silica gel.

(iii) *Preparation of* N-*t-butylbiphenyl-2-ylaminoxyl* [*Radical* (**2**)]. A solution of 2-bromobiphenyl (6.3 g) in tetrahydrofuran (THF) (10 cm^3) was gradually added to a mixture of THF (30 cm^3) and magnesium (1 g). MNP (2.3 g) in THF (10 cm^3) was then added and the solution was kept for 1 h while being stirred. After the addition of aqueous ammonium chloride, the organic layer was separated. Oxidation of this solution with an excess of lead dioxide gave a red solution of radical (**2**) which was purified by column chromatography (silica gel column, 1.5 × 20 cm) with benzene. The structure was determined by ^1H, ^{13}C NMR and mass spectroscopy. The NMR spectrum of the corresponding hydroxylamine (the conversion procedure is described later) exhibited several peaks; δ_H(400 MHz; $CDCl_3$, TMS), 0.85 (9 H, s, Bu^t), 4.65 (1 H, br, NOH), and 7.1–7.7 (9 H, m, Ar); δ_C(100 MHz; $CDCl_3$, TMS), 25 [$C(C^*H_3)_3$], 62 [$C^*(CH_3)_3$], 125–132 (C-3 to C-6, C-8 to C-12), 139, 142 (C-2, C-7), and 147 (C-1). The mass spectrum showed the following abundant fragment peaks; *m/z* 241 (M^+, 11.3%), 185 (41.5), 168 (100), 57 (45.3) and those of the aminoxyl radical were *m/z* 240 (M^+, 2.8%), 184 (42.5), 167 (16), 57 (100) (Calc. for the hydroxylamine: C, 79.66; H, 7.88; N, 5.81. Found: C, 79.51; H, 7.88; N, 5.74%). (Calc. for the aminoxyl radical: C, 80.00; H, 7.50; N, 5.83. Found: C, 79.75; H, 7.54; N, 5.91%).

(iv) *Reduction of the aminoxyl radical to the hydroxylamine for NMR measurement.* It is difficult to observe the NMR spectra of paramagnetic molecules due to the line-broadening arising from the interaction of the unpaired electron with nuclear spins. Structural studies on aminoxyl radicals by NMR spectroscopy have been achieved by reducing them to the corresponding hydroxylamines with hydrazine compounds.[26] The resulting hydroxylamines are, however, hardly separated from the oxidation products of hydrazine or the excess of hydrazine and thereby they give complicated NMR spectra. We found that zinc powder was a suitable reductant with which to reduce the aminoxyl group to hydroxylamine in high yield; this did not disturb NMR spectral observation. Moreover, the hydroxylamine was re-oxidized with lead dioxide to the aminoxyl radical of which the ESR spectrum was identical with the original one.

The procedure for the reduction is as follows. A benzene solution of radical (**2**) was added to a mixture of aqueous sodium hydroxide (1 mol dm^{-3}) and excess of zinc powder. After shaking this mixture for several minutes, the red colour disappeared and the ESR signal intensity was decreased by a factor of 0.05–0.01. The benzene layer was separated and evaporated *in vacuo*. The addition of a small portion of pentane to the residual oily product gave white solids of the corresponding hydroxylamine.

(v) *Preparation of* N-*t-butyl-2′,3′,4′,5′,6′-pentadeuteriobiphenyl-2-ylaminoxyl*, [*Radical* (**3**)]. 2-Bromo-2′,3′,4′,5′,6′-pentadeuteriobiphenyl was synthesized by the method described by Koreniowski.[27] The oily product was purified on a silica gel column (0.4 × 20 cm) using hexane as the eluant.

The mass spectrum showed the following fragment peaks; *m/z* 237 (M^+, 100%), 157 (64.2), and 156 (61.8).

Radical (**3**) was synthesized from the pentadeuteriobiphenyl by the same method as for the radical (**2**). The mass spectrum showed the following fragment peaks; *m/z* 245 (M^+, 6.1%), 189 (46.2), 172 (11.3), and 57 (100).

(*b*) *Spin Trapping Procedure and Radical Chromatography.*—Aryldiazonium salt (*ca.* 50 mg) was dissolved in a solution of MNP (0.05–0.01 mol dm^{-3}) in acetonitrile (2 cm^3). A small amount of sodium iodide was added to this solution when nitrogen gas was immediately evolved and the solution turned red. After the removal of the solvent *in vacuo*, the spin adducts were extracted with a small portion of benzene. The benzene solution was separated on a silica gel column (0.4 × 15 cm) using a hexane–benzene mixed solvent as the eluant. The flow of eluant was accelerated with air or nitrogen gas in order to perform the separation in several minutes. TLC was also used to separate the spin adducts.

(*c*) *ESR Measurements and Spectrum Treatments.*—An ESR spectrum was obtained using a JEOL PE-3X, X band ESR spectrometer. Sample solutions were carefully deaerated by bubbling nitrogen gas through the solution and by several freeze–pump–thaw cycles. The procedure for data acquisition and spectral analysis has been described.[8]

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References

1 (*a*) E. G. Janzen and B. J. Blackburn, *J. Am. Chem. Soc.*, 1968, **90**, 5909; (*b*) G. R. Chalfont, M. J. Perkins, and A. Horsfield, *ibid.*, 1968, **90**, 7141; (*c*) S. Forshult, C. Lagercrantz, and K. Torssell, *Acta Chem. Scand.*, 1969, **23**, 522; (*d*) I. H. Leaver and G. C. Ramsay, *Tetrahedron*, 1969, **25**, 5669; (*e*) S. Terabe and R. Konaka, *J. Am. Chem. Soc.*, 1969, **91**, 5655.
2 H. Taniguchi and H. Hatano, *Chem. Lett.*, 1974, 531.
3 (*a*) K. Makino, F. Moriya, and H. Hatano, *J. Chromatogr.*, 1985, **332**, 71, and references therein; (*b*) K. Makino, M. M. Mossoba, and P. Riesz, *Radiat. Res.*, 1983, **96**, 416; (*c*) T. I. Ho, C. M. Chang, S. R. Wang, and C. P. Chem, *J. Chem. Soc., Dalton Trans.*, 1988, 123; (*d*) T. I. Ho, K. Nozaki, A. Naito, S. Okazaki, and H. Hatano, *J. Chem. Soc., Chem. Commun.*, 1989, 206.
4 E. G. Janzen, *Acc. Chem. Res.*, 1971, **4**, 31.
5 (*a*) C. Galli, *Chem. Rev.*, 1988, **88**, 765; (*b*) H. Zollinger, *Acc. Chem. Res.*, 1973, **6**, 335; (*c*) H. Zollinger, *Angew. Chem.*, 1978, **17**, 141; (*d*) H. Zollinger, *Helv. Chim. Acta*, 1981, **64**, 488.
6 (*a*) R. G. Gasanov, B. V. Kopylova, L. V. Yashkina, and R. Kh. Freidlina, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1982, **8**, 1915; 1983, **5**, 1190; (*b*) A. J. Bard, J. C. Gilbert, and R. D. Goodin, *J. Am. Chem. Soc.*, 1974, **96**, 620.
7 (*a*) F. P. Sargent and E. M. Gardy, *J. Chem. Phys.*, 1977, **67**, 1793; (*b*) J. C. Bevington, P. F. Fridd, and B. J. Tabner, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1389.
8 K. Nozaki, A. Naito, H. Hatano, and S. Okazaki, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 1715.
9 A. R. Forrester, J. M. Hay, and R. H. Thomson, 'Organic Chemistry of Stable Free Radicals,' Academic Press, New York, 1968, ch. 5.
10 J. C. Baird and J. R. Thomas, *J. Chem. Phys.*, 1961, **35**, 1507.
11 H. Lemaire, Y. Marechal, R. Ramasseul, and A. Rassat, *Bull. Soc. Chim. Fr.*, 1965, 372.
12 J. A. Pedersen and K. Torssell, *Acta Chem. Scand.*, 1971, **25**, 3151.
13 A. Calder, A. R. Forrester, J. W. Emsley, G. R. Luckhurst, and R. A. Storey, *Mol. Phys.*, 1970, **18**, 481.
14 H. J. Jakobsen, T. E. Petersen, and K. Torssell, *Tetrahedron Lett.*, 1971, **31**, 2913.
15 H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, 1958, **28**, 107.
16 J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw–Hill, New York, 1970.
17 A. R. Forrester and R. H. Thomson, *Nature (London)*, 1964, **203**, 74.
18 H. Wieland and K. Roth, *Ber.*, 1920, **53**, 210.
19 A. R. Forrester and S. P. Hepburn, *J. Chem. Soc. C*, 1970, 1277.
20 A. Alberti, L. Greci, P. Stipa, P. Sgarabotto, and F. Vgozzoli, *Tetrahedron*, 1987, **43**, 3031.
21 A. Calder and A. R. Forrester, *J. Chem. Soc. C*, 1969, 1459.
22 A. R. Forrester and S. P. Hepburn, *J. Chem. Soc., Perkin Trans. 1*, 1974, 2208.
23 J. C. Stowell, *J. Org. Chem.*, 1971, **36**, 3055.
24 A. K. Hoffmann, A. M. Feldman, and E. Gelblum, *J. Am. Chem. Soc.*, 1964, **86**, 646.
25 R. H. Bullard and J. B. Dickey, *Org. Synth.*, 1943, **2**, 494.
26 T. D. Lee and J. F. W. Keana, *J. Org. Chem.*, 1975, **40**, 3145.
27 S. H. Korzeniowski, L. Blum, and G. W. Gokel, *Tetrahedron Lett.*, 1977, **22**, 1871.

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