Exceptionally Persistent Nitrogen-Centered Free Radicals. Syntheses, ESR Spectra, Isolation, and X-ray Crystallographic Structures of *N*-(Arylthio)-2-*tert*-butyl-4,6-diarylphenylaminyl and *N*-(Arylthio)-4-*tert*-butyl-2,6-diarylphenylaminyl Radicals[1]

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The preparation, ESR spectra, isolation, and X-ray crystallographic structure of *N*-(arylthio)-2-*tert*-butyl-4,6-diarylphenylaminyls (**1**) and *N*-(arylthio)-4-*tert*-butyl-2,6-diarylphenylaminyls (**2**) are described. The aminyls are generated by PbO_2 oxidation of *N*-(arylthio)-2-*tert*-butyl-4,6-diarylanilines and *N*-(arylthio)-4-*tert*-butyl-2,6-diarylanilines. The kinetic ESR study shows that the aminyls are quite persistent, even in the presence of oxygen, and exist in the individual radical forms. Among the seventeen aminyls prepared, *N*-[(4-nitrophenyl)thio]-2-*tert*-butyl-4,6-diphenylphenylaminyl (**1b**), *N*-[(4-nitrophenyl)thio]-2-*tert*-butyl-4,6-bis(4-chlorophenyl)phenylaminyl (**1f**), *N*-[(4-nitrophenyl)thio]-4-*tert*-butyl-2,6-diphenylphenylaminyl (**2b**), *N*-[(4-nitrophenyl)thio]-4-*tert*-butyl-2,6-bis(4-chlorophenyl)phenylaminyl (**2h**), and *N*-[(3,5-dichlorophenyl)thio]-4-*tert*-butyl-2,6-bis(4-chlorophenyl)phenylaminyl (**2j**) are isolated as radical crystals. The crystallographic structures of **1b** and **2b** are determined by the X-ray crystallographic analyses. Aminyls **1** and **2** give similar ESR spectra consisting of 1:1:1 triplets with the a_N values of 0.921−0.948 mT. Deuteration of the phenyl groups on the anilino benzene ring gives rise to a further splitting of the nitrogen 1:1:1 triplet by the anilino meta (0.126−0.138) and phenylthiyl ortho and para protons (0.077−0.096 mT). Upon recording at high gain, one of the partly deuterated aminyls gives satellite lines due to ^{33}S isotopes at natural abundance from which a^{33}_S is determined to be 0.51 mT. The ESR parameters for **1** and **2** are compared with those for structurally close *N*-(arylthio)-2,4,6-triarylphenylaminyl and *N*-(arylthio)-2,4,6-tri-*tert*-butylphenylaminyl.

Introduction

For recent years the chemistry of stable free radicals have been largely stimulated by the expectation that organic free radicals might have ferromagnetic properties. Many free radical crystals have widely been investigated from the view points of the purely organic magnetism.[2] Some radical crystals including 2-(*p*-nitrophenyl)nitronyl nitroxide have found to be purely organic ferromagnets at very low temperatures.[3] However, most of the stable free radicals investigated have been limited to nitroxides and nitronyl nitroxides which have a localized electron spin because they can be easily prepared and have an exceptional stability. Therefore, the quest of a new class of stable free radicals has been strongly desired for the further advances in chemistry and physics of purely organic magnetism. Standing on this background, we have made an effort to search for a new class of stable free radicals as a part of a program directed toward the syntheses of high-spin or ferromagnetic materials.[1,4] Our extensive studies on thioaminyls (R′ṄSR) (Chart 1) have shown that *N*-(arylthio)-2,4,6-triarylphenylaminyls (**3**) are exceptionally persistent and can be isolated as pure radical crystals.[5] Their magnetic studies have shown that, although most **3** couples antiferromagnetically in the crystal state, three thioaminyls couple ferromagnetically with the J_1/k values of 1.8−14.0 K.[6,7] As an extension of this study we have investigated *N*-(arylthio)-2-*tert*-butyl-4,6-diarylphenylaminyls (**1**) and

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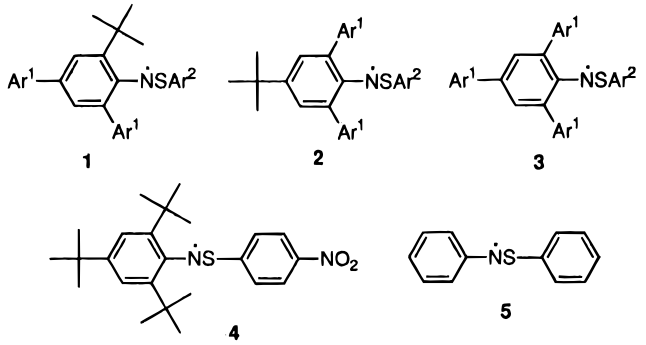
Chart 1



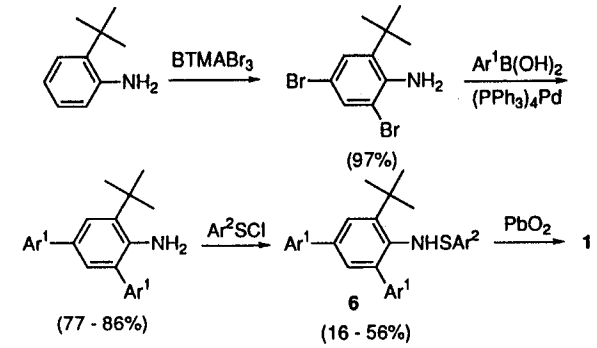
N-(arylthio)-4-*tert*-butyl-2,6-diarylphenylaminyls (**2**).[8] As shown by their structures, aminyls **1** and **2** are analogues of **3**: one of three aryl groups at the 2,4,6-positions of the anilino group is replaced by a *tert*-butyl group. Although the *tert*-butyl group is superior as a protecting group, it has no ability to stabilize the aminyls electronically. Nevertheless, our ESR study on **1** and **2** has shown that they are quite persistent and some can be isolated as radical crystals. In this paper we report on the generation, ESR spectra, isolation, and X-ray crystallographic structures of **1** and **2**.

Results and Discussion

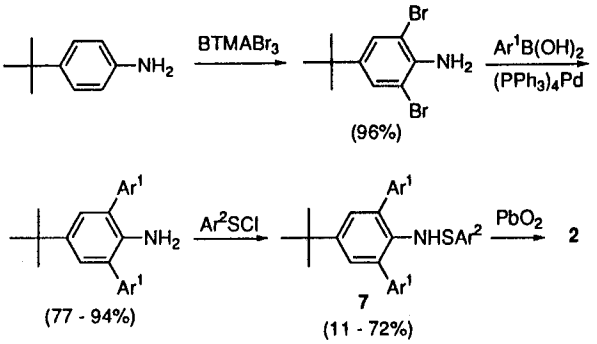
Syntheses of Precursors 6 and 7. The syntheses of *N*-(arylthio)-2-*tert*-butyl-4,6-diarylanilines (**6**) and *N*-(arylthio)-4-*tert*-butyl-2,6-diarylanilines (**7**) were performed according to Scheme 1. Thus, treatment of 2- and 4-*tert*-butylaniline with benzyltrimethylammnonium tribromide (BTMA Br_3) in CH_3OH in the presence of $CaCO_3$ gave 2-*tert*-butyl-4,6-dibromoaniline and 4-*tert*-butyl-2,6-dibromoaniline in 97 and 96% yields,[9] respectively. The bromoanilines were then subjected to the palladium-catalyzed cross-coupling reaction with 2 equiv of phenylboronic acid or 4-chlorophenylboronic acid (Suzuki reaction[10]) to yield the corresponding 2-*tert*-butyl-4,6-diarylaniline and 4-*tert*-butyl-2,6-diarylaniline in 77−86 and 77−94% yields,[9] respectively. The reactions of 2-*tert*-butyl-4,6-diarylanilines or 4-*tert*-butyl-2,6-diarylanilines with arenesulfenyl chlorides in dry ether in the presence of Et_3N gave **6** and **7** in 16−50 and 11−72% yields, respectively, after chromatographic separation and subsequent crystallization. The crystals of **6** and **7** isolated often showed a light green or purple color, even after recrystallization. This was ascribed to the contamination with **1** or **2** generated during recrystallization.

Generation and ESR Spectra of 1 and 2 Radicals. Aminyls **1** and **2** were generated by oxidation of **6** and **7** with PbO_2 in benzene. When PbO_2 was added to a stirred solution of **6** or **7** in benzene, the solutions turned green, blue, purple, or wine-red and gave an intense 1:1:1 triplet ESR spectrum. In most cases the oxidation was fast and the color change occurred immediately. However, in the cases of Ar^2 = 2,4-$Cl_2C_6H_3$ (**6c**, **6g**, **7c**, and **7i**), it was slow; in particular, **6c** and **6g**. Therefore, the color changes occurred 1−3 min after addition of PbO_2. The

Scheme 1



a: Ar^1 = Ph, Ar^2 = 3-$NO_2C_6H_4$ **e**: Ar^1 = 4-ClC_6H_4, Ar^2 = 3-$NO_2C_6H_4$
b: Ar^1 = Ph, Ar^2 = 4-$NO_2C_6H_4$ **f**: Ar^1 = 4-ClC_6H_4, Ar^2 = 4-$NO_2C_6H_4$
c: Ar^1 = Ph, Ar^2 = 2,4-$Cl_2C_6H_3$ **g**: Ar^1 = 4-ClC_6H_4, Ar^2 = 2,4-$Cl_2C_6H_3$
d: Ar^1 = Ph, Ar^2 = 3,5-$Cl_2C_6H_3$



a: Ar^1 = Ph, Ar^2 = 3-$NO_2C_6H_4$ **f**: Ar^1 = Ph, Ar^2 = 4-BrC_6H_4
b: Ar^1 = Ph, Ar^2 = 4-$NO_2C_6H_4$ **g**: Ar^1 = 4-ClC_6H_4, Ar^2 = 3-$NO_2C_6H_4$
c: Ar^1 = Ph, Ar^2 = 2,4-$Cl_2C_6H_3$ **h**: Ar^1 = 4-ClC_6H_4, Ar^2 = 4-$NO_2C_6H_4$
d: Ar^1 = Ph, Ar^2 = 3,5-$Cl_2C_6H_3$ **i**: Ar^1 = 4-ClC_6H_4, Ar^2 = 2,4-$Cl_2C_6H_3$
e: Ar^1 = Ph, Ar^2 = 4-ClC_6H_4 **j**: Ar^1 = 4-ClC_6H_4, Ar^2 = 3,5-$Cl_2C_6H_4$

reason why the oxidation is slow for such precursors is not obvious. A typical ESR spectrum of **2c** is shown in Figure 1, and the ESR parameters are summarized in Table 1.

The ESR spectra of most radicals are a simple 1:1:1 triplet split by the interaction with the ^{14}N nucleus, with a relatively large peak-to-peak width (~0.13 mT) due to the presence of numerous unresolved proton hyperfine splittings. In the cases of **1g**, **2d**, and **2f** the 1:1:1 triplet spectra were further split by the interaction with aromatic protons, but their hyperfine resolutions were quite poor. Only two exceptions are **2c** and **2i**. In their ESR spectra the 1:1:1 triplet was further split with a relatively good resolution by the interaction with the two anilino meta and one arylthiyl ortho protons, as shown in Figure 1. The magnitudes of the proton hfs constants were determined by computer simulation and assigned on the basis of the ESR results of partly deuterated thioaminyls **8** and **9** as described below.

Furthermore, we tried to detect ^1H ENDOR signals for some aminyl radicals to ascertain the proton hfc constants for **1** and **2**. Among the aminyls examined, only **2b** gave an ENDOR spectrum upon the measurements at −75 °C using toluene, after 400 accumulations. As shown in Figure 2, three pairs of signals were observed from which the proton hfc constants of 0.123, 0.0776, and 0.0184 mT were determined. Based on the ESR results of the partly deuterated aminyls, 0.123, 0.0776, and 0.0184 mT were, respectively, assigned to the anilino meta, arylthiyl ortho, and arylthiyl meta protons.

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(10) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

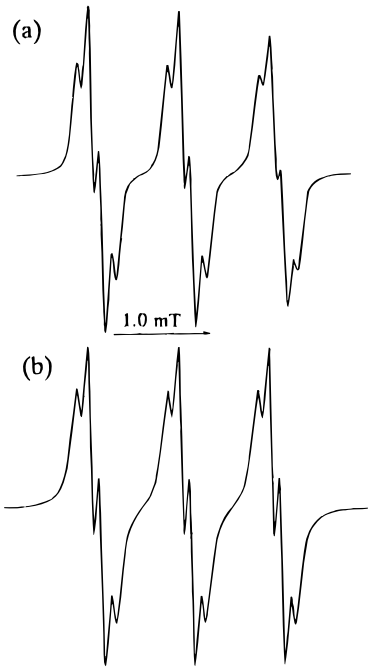


Figure 1. Experimental (a) and computer-simulated (b) ESR spectra of **2c**. The experimental ESR spectrum was obtained at 20 °C using benzene as solvent.

Table 1. ESR Parameters for 1 and 2 in Benzene at 20 °C[a]

radical	a_N	g
1a	0.932	2.0054
1b	0.937	2.0055
1c	0.948	2.0056
1d	0.936	2.0054
1e	0.933	2.0057
1f	0.937	2.0056
1g	0.953	2.0058
2a	0.936	2.0055
2b[b]	0.932	2.0055
2c[c,d]	0.936	2.0056
2d	0.932	2.0054
2e	0.934	2.0058
2f	0.933	2.0060
2g	0.931	2.0057
2h	0.930	2.0056
2i[c,e]	0.936	2.0057
2j	0.921	2.0055

[a] The hyperfine coupling constants are given in mT. [b] The ^{1}H ENDOR spectrum of **2b** in toluene obtained at −75 °C gave the proton hfc constants of 0.123 (anilino meta), 0.0776 (arylthiyl ortho), and 0.0184 mT (arylthiyl meta). [c] The proton hfc constants were determined by computer simulation. [d] The other hfc constants determined: 0.125 mT (2H) (anilino meta); 0.096 mT (1H) (arylthiyl ortho). [e] The other hfc constants determined: 0.123 mT (2H) (anilino meta); 0.096 mT (1H) (arylthiyl ortho).

As found in Table 1, the a_N values for **1** and **2** are almost constant, regardless of the position of the *tert*-butyl group and the electronic characters of the substituent(s) on the 2,4- and 2,6-diphenyl and phenylthiyl groups. This indicates that the relative importance of the canonical structures A and B are not changed by the electronic characters of the substituents and that the conformation of **1** and **2** are not affected by the position of the *tert*-butyl group.

Generation and ESR Spectra of Partly Deuterated Radicals 8 and 9. It is essential for the evaluation of the spin density distribution to precisely determine the proton hfc constants as well as the nitrogen hfc constants. Although, for **2c** and **2i** the proton hfc constants for the

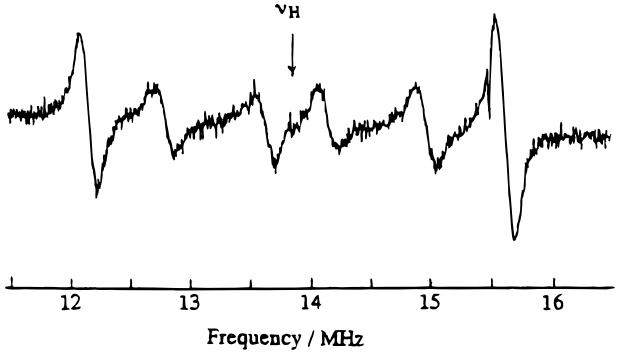


Figure 2. ^{1}H ENDOR spectrum of **2b** recorded at −75 °C using toluene as solvent.

Scheme 2

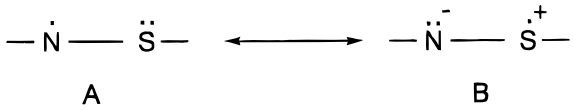
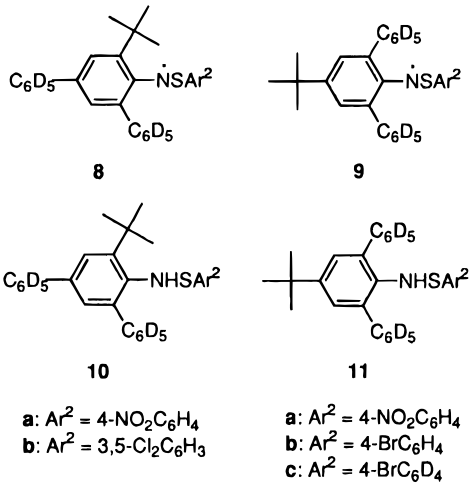


Chart 2



anilino meta and arylthiyl ortho protons could be determined, their unequivocal assignments were impossible unless either the anilino benzene ring or the arylthiyl group was deuterated. We therefore prepared partly deuterated thioaminyls, **8** and **9** (Chart 2). The corresponding precursors **10** and **11** were prepared by the reaction of 2,4-di(phenyl-d_5)-6-*tert*-butylaniline or 2,6-di(phenyl-d_5)-4-*tert*-butylaniline with arenesulfenyl chlorides according to the same procedure as for the corresponding nondeuterated compounds. The radicals were generated by the same procedure as for nondeuterated radicals. Typical ESR spectra are shown in Figures 3 and 4, and their ESR parameters are summarized in Table 2.

As found in the Figure 3, the partly deuterated aminyls gave a well resolved ESR spectra with a small line width. However, the ESR spectra of **8a** and **9a** were considerably broader than those of the other deuterated thioaminyls, probably due to the presence of the unresolved nitro group nitrogen hyperfine splitting.

Interestingly, in the ESR spectrum of **9c** satellite lines due to ^{33}S at natural abundance (0.75%), together with satellite lines due to ^{13}C at natural abundance (1.11%), were observed in the wings where the spectra were recorded at high gain (Figure 4). The assignments of these satellites were made by the intensity ratio of the

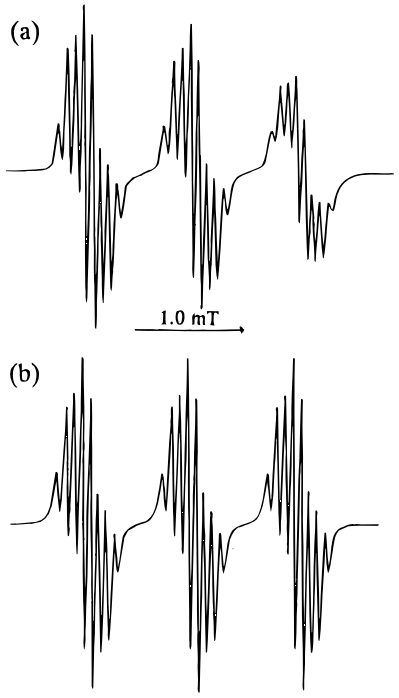


Figure 3. Experimental (a) and computer-simulated (b) ESR spectra of **8b**. The experimental spectrum was obtained at 20 °C using benzene as solvent.

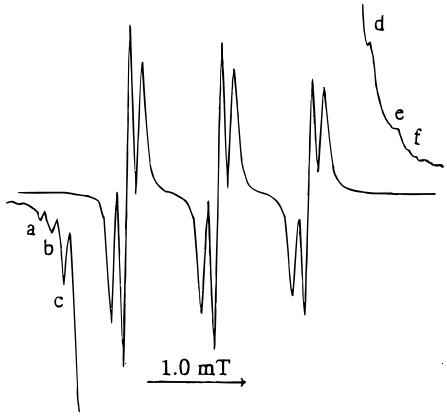


Figure 4. Experimental ESR spectrum of **9c** recorded at 20 °C using benzene as solvent. Both wings are recorded at high gain (100 times). Satellite lines due to ^{33}S (a and b, $M_N = +1$, $M_S = +^3/_2$; e and f, $M_N = -1$, $M_S = -^3/_2$) and ^{13}C isotopes (c, $M_N = +1$, $M_C = +^1/_2$; d, $M_N = -1$, $M_C = -^1/_2$) are found.

Table 2. ESR Parameters for 8 and 9 in Benzene at 20 °C[a]

radical	a_N	a_{other}	g
8a[b]	0.935	0.127 (2H),[c] 0.077 (2H)[d]	2.0055
8b[b]	0.937	0.138 (2H),[c] 0.078 (3H)[d]	2.0054
9a[b]	0.933	0.126 (2H),[c] 0.083 (2H)[d]	2.0055
9b	0.932	0.130 (2H),[c] 0.085 (2H)[d]	2.0060
9c	0.934	0.130 (2H),[c] 0.51 (^{33}S),[e] 1.01 ($1^{13}C$)[f]	2.0060

[a] The hyperfine coupling constants are given in mT. [b] The hfc constants are determined by computer simulation. [c] The hfc constants for the anilino meta protons. [d] The hfc constants for the arylthiyl ortho and para protons. [e] The value is determined by the satellite lines due to ^{33}S at natural abundance. [f] The value is determined by the satellite lines due to ^{13}C at the natural abundance.

satellite lines to the parent spectrum. Since the ^{33}S ($I = ^3/_2$) and ^{13}C ($I = ^1/_2$) isotope percents are 0.76 and 1.11, respectively, the theoretical values of the intensity ratios of the satellite lines due to ^{33}S and ^{13}C at natural abundance to the parent spectrum are 0.19 and 0.56%, respectively. On the other hand, the observed intensity ratio of the ^{33}S satellites to the parent spectrum was 0.13% and that of the ^{13}C satellites was 0.40%, which were close to the theoretical values.

Isolation of 1 and 2. Aminyls **1** and **2** were quite persistent, even in the presence of atmospheric oxygen. The stabilities of **1** and **2** were evaluated by following the radical concentrations by double-integration of ESR spectra as a function of time. Although the measurements were continued for 10 h at 20 °C under atmospheric conditions, no reduction in the radical concentrations was observed. Furthermore, the aminyls showed no tendency to dimerize, upon cooling to low temperatures, exhibiting that the aminyls existed in the individual radical form in solution. On the basis of these observations we decided to try to isolate the aminyls.

Isolation of **1** and **2** was carried out as follows: precursors **6** and **7** were treated with PbO_2 in benzene, and the solvent was removed by freeze-drying. The resulting dark brown or green crystalline powder residue was crystallized from hexane, hexane−ethyl acetate, or ethanol. Among the 17 radicals prepared, **1b**, **1f**, **2b**, **2h**, and **2j** were successfully isolated as black (dark brown) needles or prisms in 33−56% yields. In the unsuccessful cases, on the other hand, the PbO_2 oxidation of the precursors yielded large amounts of unknown polar byproducts.[11] Note that the radicals isolated have one or more electron-withdrawing substituent on the 2,4,6-triphenyl and arylthiyl groups. We explain this result as follows: introduction of one or more π electron-withdrawing substituent reduce the lone pair−lone pair repulsion between N and S of the precursors, strengthening the N−S bond. Therefore, we understand that the N-S bond cleavage of **6** and **7** upon oxidation leading to the polar byproducts takes place to a much less extent and the suppression of the N−S bond cleavage allows us to isolate **1b**, **1f**, **2b**, **2h**, and **2j** as pure radical crystals. The isolated radical crystals were very stable and showed no decomposition upon storage at 0 °C.

X-ray Crystallographic Analysis. Upon recrystallization from ethanol (**1b)** or hexane (**2b**), a sufficiently large single crystal suitable for X-ray crystallographic analysis was provided. Figures 5 and 6 show the ORTEP drawings of the molecular structures of **1b** and **2b**. The selected bond lengths, bond angles, and dihedral angles are summarized in Table 3.

The X-ray crystallographic analysis of **1b** shows the following structural feature: the N and S atoms are coplanar with the benzene ring A. This planar group makes a dihedral angle of 21° with the benzene ring D. The dihedral angle between the benzene rings A and C is 34°, while that between the benzene rings A and B is 87°, indicating that there are serious steric congestions around the N−S bond surrounded by a phenyl group and a *tert*-butyl group. On the other hand, the X-ray results of **2b** give the following structural features. The N and S atoms are coplanar with the benzene ring D (not A), and this planar group makes a dihedral angle of 21° with the benzene ring A. The benzene ring A makes a dihedral angles 64° with the benzene ring B and 45° with the benzene ring C. Therefore, the steric congestions around the N−S bond surrounded by the two benzene

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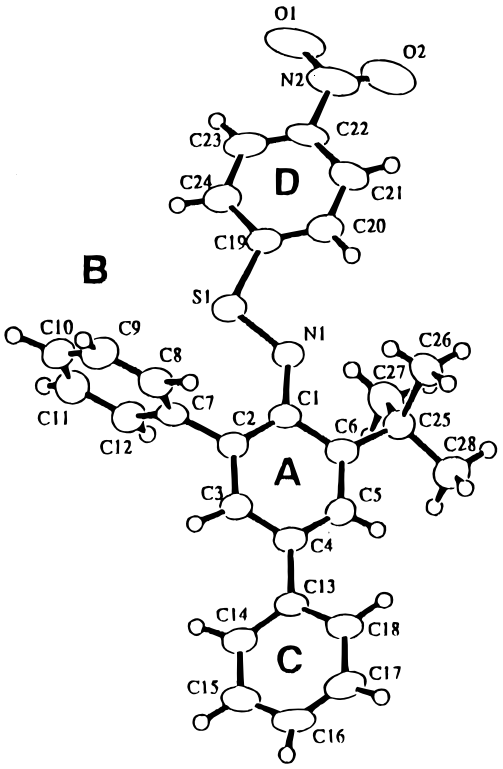


Figure 5. ORTEP drawing of **1b**.

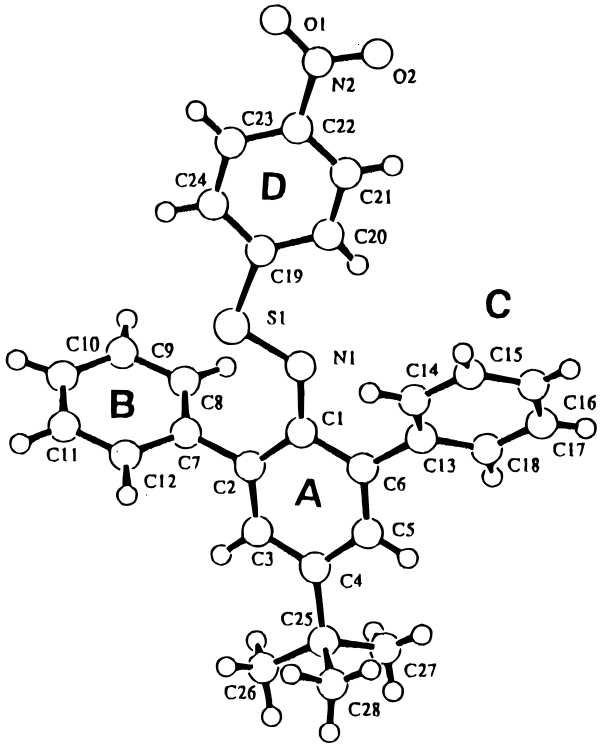


Figure 6. ORTEP drawing of **2b**.

rings are serious, but less so than in **1b**. On the basis of the above X-ray results it is concluded that both radicals have an approximately planar π-framework consisting of the A and D benzene rings and N and S atoms. However, the ortho-substituted phenyl group(s) are twisted from the A benzene ring. Accordingly, the unpaired electron can extensively delocalize from the nitrogen to the anilino and phenylthiyl groups, but cannot delocalize to the ortho benzene ring(s). This

Table 3. Selected Bond Lengths and Angles and Dihedral Angles for 1b and 2b

1b

Bond Lengths (Å)		Bond Angles (deg)	
C1−N1	1.382 (5)	C2−C1−N1	125.9 (4)
N1−S1	1.618 (3)	C6−C1−N1	114.2 (3)
S1−C19	1.780 (4)	C1−N1−S1	123.4 (3)
		N1−S1−C19	100.3 (2)

Dihedral Angles (deg)

S1−N1−C1−C2	−5.8 (5)	N1−S1−C19−C20	−18.0 (4)
S1−N1−C1−C6	173.7 (3)	N1−S1−C19−C24	161.5 (3)
C1−N1−S1−C19	−177.7 (3)		

2b

Bond Lengths (Å)		Bond Angles (deg)	
C1−N1	1.384 (3)	C2−C1−N1	126.8(2)
N1−S1	1.616 (2)	C6−C1−N1	115.4(2)
S1−C19	1.750 (3)	C1−N1−S1	121.7(2)
		N1−S1−C19	101.1(1)

Dihedral Angles (deg)

S1−N1−C1−C2	22.4 (3)	N1−S1−C19−C20	2.4(3)
S1−N1−C1−C6	−158.1 (2)	N1−S1−C19−C24	−178.7(2)
C1−N1−S1−C19	175.3 (2)		

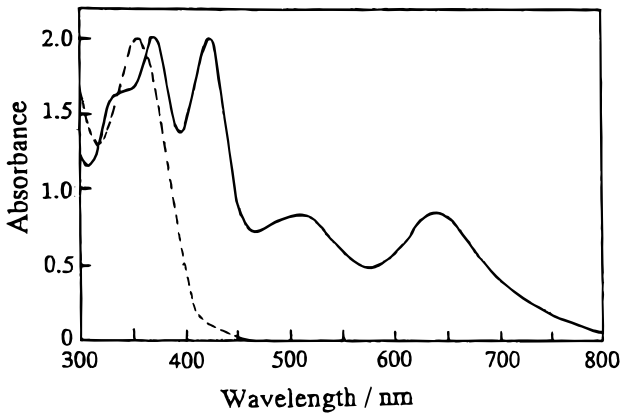


Figure 7. UV-vis spectra of **1b** and **6b** in benzene: (—) **1b**, 1.49×10^{-4} M; (- - - -) **6b**, 1.49×10^{-4} M.

conclusion is in accordance with the ESR results that show an extensive delocalization of the unpaired electron spin to the anilino and phenylthiyl benzene rings.

UV-vis Spectra. Aminyls **1** and **2** are characterized by a green (**1a**−**g**), blue (**2c**, **2e**, **2f**, **2i**), purple (**2a**, **2b**, **2d**, **2j**), purplish blue (**2g**), or dark wine-red color (**2h**). The UV-vis spectra of **1b**, together with the corresponding precursor **6b** are illustrated in Figure 7, and the UV-vis absorption data for **1** and **2** are summarized in Table 4.

As shown by Figure 7, aminyl **1b** shows the absorption peaks attributable to the characteristic green color at 641 (ϵ 5750), 512 (5600), and 424 nm (13400). The large ϵ values indicate that the absorptions are due to the $\pi-\pi$ transitions. On the other hand, **6b** absorbs only at 355 nm (ϵ 13000) in the UV-vis region. Likewise, the other aminyls also show the absorption peaks corresponding to the characteristic color in the visible region from which their presence can be readily recognized.

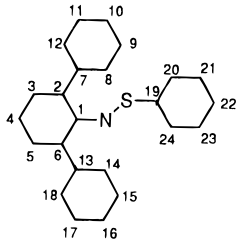
Spin Density Distribution. The spin density distribution in **2** was elucidated by the Hückel and McLachlan−Huckel molecular orbital (MO) calculations using the following parameters: $\alpha_N = \alpha + 0.6\beta$, $\alpha_S = \alpha + \beta$, $\beta_{CN} = 1.1\beta$, $\beta_{NS} = 0.7\beta$, $\beta_{CS} = 0.7\beta$, $\lambda = 0.7$. The set of parameters have been always employed in our calculations on thioaminyl radicals.[12] The Coulomb integrals between C2−C7 and C6−C13 are changed as follows on

Table 4. UV-Vis Spectral Data for 1 and 2 in Benzene[a]

radical	l_{max}, nm (e, L mol^{-1} cm^{-1})
1a	632, 521 (sh)
1b	641 (5750), 512 (5600), 424 (13400), 370 (13600), 338 (sh, 11100)
1c	645, 530 (sh)
1d	633, 528 (sh)
1e	638, 525 (sh)
1f	647 (6440), 503 (sh, 5740), 428 (16100), 375 (16900)
1g	652, 530 (sh)
2a	579, 501
2b	583 (6000), 492 (9690), 387 (12500), 309 (11300)
2c	593, 527 (sh)
2d	580, 518 (sh)
2e	594, 520 (sh)
2f	595, 522 (sh)
2g	583, 502 (sh), 366
2h	594 (5590), 485 (8130), 387 (12000), 306 (10700)
2i	599, 525 (sh), 374
2j	584 (6440), 522 (sh, 3530), 373 (13100)

[a] For the isolated radicals, the ϵ values are given in parentheses.

Table 5. Experimental and Calculated Hyperfine Coupling Constants for 2



position	obsd hfc const[a]	calcd spin density	calcd hfc const[a,b]
N	0.932 (N)[c]	0.495	1.09 (N)
S	0.51 (^{33}S)[d]	0.203	0.467 (S)
1		−0.042	
2		0.119	
3	0.123 (H)[c]	−0.029	0.078 (H)
4		0.111	
5		−0.029	
6		0.116	
7		−0.001	
8, 12		0.001	
9, 11		−0.000	
10		0.001	
13		−0.003	
14, 18		0.007	
15, 17		−0.002	
16		0.006	
19		−0.012	
20, 24	0.0776 (H)[c]	0.024	−0.065 (H)
21, 23	0.0184 (H)[c]	−0.008	0.022 (H)
22		0.022	

[a] Hyperfine coupling constants are given in mT. [b] Derived using equation, $a_X = Q_X\rho_X$, where $Q_H = -2.7$, $Q_N = 2.2$, $Q_{33_S} = 2.3$ mT.[12] [c] The values for **2b** determined by ^{1}H ENDOR. [d] The value for **9c**.

the basis of the X-ray results: $\beta_{C2-C7} = (\cos^2 64°)\beta = 0.192\beta$, $\beta_{C6-C13} = (\cos^2 45°)\beta = 0.500\beta$. As found in Table 5, the calculations agree well with the experimental data, predicting that there is an extensive delocalization of the unpaired electron spin onto the anilino and phenylthiyl groups, in accordance with the ESR results. On the other hand, the delocalization of the unpaired electron spin onto the 2- and 6-phenyl groups is negligibly small due to their twisting.

Table 6. Comparison of ESR Parameters of 1−4[a]

radical	a_N	a_H[b]	a^{33}_S	g
1 (and **8**)	0.932−0.953	0.127−0.138		2.0054−2.0058
2 (and **9**)	0.921−0.936	0.123−0.130	0.51	2.0055−2.0060
3	0.890−0.896	0.133 −0.134	0.51	2.0054−2.0059
4	1.230			2.0066
5	0.959	0.126		2.0059

[a] The hyperfine coupling constants are given in mT. [b] The value for the anilino meta protons.

The spin density distribution in **1** was also elucidated. As shown by the ESR results of the aminyls shown in Tables 1 and 2, the a_N and a_H values for **1** and **8** are very similar to those for **2** and **9**. Therefore, it can be concluded that the spin density distributions in **1** and **2** are very similar to each other, and this was supported by the McLachlan−Hückel MO calculations of **1** and the crystallographic results which show a similar conformation for **1** and **2**.

Comparison of Hyperfine Coupling Parameters. Aminyls **1** and **2** are structurally close to **3**, **4**, and **5**. Their ESR parameters are compared in Table 6. It was previously reported that, although unsubstituted **5** was quite unstable and its isolation was impossible,[13] aminyls **3** and **4** were quite stable and could be isolated as radical crystals.[14,15] Among the isolable aminyls **1**, **2**, **3**, and **4**, only **4** reacts with oxygen to decompose to nonradical compounds.[14] This oxygen-sensitive property of **4** was ascribed to its twisted conformation clarified by the X-ray crystallographic analysis showing that the anilino group make a dihedral angle of 91° for the planar group consisting the N atom and phenylthiyl group. Therefore, an electronic stabilization by the anilino group cannot be expected. On the other hand, **1**, **2**, and **3** adopt a nearly planar conformation, as shown by their X-ray crystallographic analyses. Accordingly, the ESR parameters (a and g) for **1**, **2**, and **3** are very similar to each other and also similar to those for **5**. However, their ESR parameters are quite different from those of **4** adopting a twisted conformation.

Conclusions. Thioaminyl radicals **1** and **2** were generated by PbO_2 oxidation of the corresponding precursors. The ESR studies showed they are quite persistent even in the presence of oxygen and exist in the individual radical form. Isolation of the aminyls was attempted and five radicals were obtained as pure radical crystals. The X-ray crystallographic analyses showed that both **1** and **2** adopt a similar planar conformation, in accordance with the ESR results showing that the unpaired electron is extensively delocalized from the nitrogen to the anilino and arylthiyl groups.

The magnetic susceptibility measurements for the isolated thioaminyls are in progress and the results will be published elsewhere.

Experimental Section

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. The IR, UV-visible, and ^{1}H NMR spectra were recorded as previously reported.[15]

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(13) Miura, Y.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1142.

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(15) Miura, Y.; Tanaka, A.; Hirotsu, K. *J. Org. Chem.* **1991**, *56*, 6638.

4-Chloro-, 4-bromo-, 2,4-dichloro-, 3,5-dichloro-, 3-nitro-, and 4-nitrobenzenesulfenyl chlorides were obtained by the usual method.[16,17] The preparation of 4-bromobenzenesulfenyl-d_4 chloride is described in our previous report.[15] Phenylboronic-d_5 acid was obtained by the reaction of phenylmagnesium-d_5 bromide with trimethoxyboron, followed by hydrolysis, according to the procedure for the corresponding nonlabeled compound.

2-*tert*-Butyl-4,6-diphenylaniline and 4-*tert*-butyl-2,6-diphenylaniline were obtained by the Pd-catalyzed cross coupling reaction (Suzuki reaction) of 2-*tert*-butyl-4,6-dibromoaniline or 4-*tert*-butyl-2,6-dibromoaniline with phenylboronic acid according to our previously reported method.[9]

4-*tert*-Butyl-2,6-bis(4-chlorophenyl)aniline. By the same procedure as for 4-*tert*-butyl-2,6-diphenylaniline, 4-*tert*-butyl-2,6-dibromoaniline (5.93 g, 19.3 mmol) was treated with 9.05 g (57.9mmol) of 4-chlorophenylboronic acid in the presence of 2.68 g (2.32 mmol) of $(PPh_3)_4Pd$ and 16.4 g of Na_2CO_3 in a benzene (200)−ethanol (40)−water (75 mL) mixed solvent at the reflux temperature for 24 h under nitrogen. After the usual workup, the reaction mixture was chromatographed on silica gel (Wako gel C200) with 1:1 benzene−hexane as eluant. Crystallization from hexane gave colorless needles with mp 189−191 °C in 77% yield: ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 9 H), 3.66 (s, 2 H), 7.12 (s, 2 H), 7.43 (d, J = 8.6 Hz, 4 H), 7.45 (d, J = 8.6 Hz, 4 H). Anal. Calcd for $C_{22}H_{21}Cl_2N$: C, 71.35; H, 5.72; N, 3.78. Found: C, 71.30; H, 5.70; N, 3.70.

2-*tert*-Butyl-4,6-bis(4-chlorophenyl)aniline. By the same procedure as for 2-*tert*-butyl-4,6-diphenylaniline, 2-*tert*-butyl-4,6-dibromoaniline (5.19 g, 16.9 mmol) was treated with 7.93 g (50.7 mmnol) of 4-chlorophenylboronic acid in the presence of 2.34 g (2.02 mmol) of $(PPh_3)_4Pd$ and 14.3 g of Na_2CO_3 in a benzene (170)−ethanol (35)−water (70 mL) mixed solvent at the reflux temperature for 24 h under nitrogen. After the usual workup, the reaction mixture was chromatograph on silica gel with 1:1 benzene−hexane as eluant. Crystallization from hexane−benzene gave colorless needles with mp 145−146 °C in 77 % yield (4.80 g, 13.0 mmol): ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 9 H), 4.01 (s, 2 H), 7.16−7.48 (m, 10 H). Anal. Calcd for $C_{22}H_{21}Cl_2N$: C, 71.35; H, 5.72; N, 3.78. Found: C, 71.25; H, 5.64; N, 3.84.

General Procedure for Preparation of *N*-(Arylthio)-2-*tert*-butyl-4,6-diarylanilines (6) and *N*-(Arylthio)-4-*tert*-butyl-2,6-diarylanilines (7). To a stirred solution of 2.00 g (6.64 mmol) of 2-*tert*-butyl-4,6-diarylaniline (or 4-*tert*-butyl-2,6-diarylaniline) and 1.46 g (14.4 mmol) of triethylamine in 200 mL of dry ether was added dropwise at 0 °C a solution of 10.0 mmol of arenesulfenyl chloride in 50 mL of dry ether. After the addition was completed, the mixture (sometime colored) was continued to stir for 2 h at 0 °C. After filtration, the filtrate was evaporated under reduced pressure, and the residue was chromatographed on alumina (Merck, aluminium oxide 90) using 2:1 (**6f**), 1:1 (**6a**, **6b**, **6e**, **7a**, **7b**, **7g**, **7h**), 1:3 (**7c**, **7d**, **7e**, **7f**), 1:5 (**6c**, **6d**, **6g**, **7j**), 1:8 benzene−hexane (**7i**) as eluant to give a pure solid or a solid containing small amounts of diaryl disulfide and/or the starting aniline. Crystallization from the appropriate solvent gave pure compounds.

***N*-[(3-Nitrophenyl)thio]-2-*tert*-butyl-4,6-diphenylaniline (6a):** yellowish green plates (ethanol); mp 138−139 °C; yield 34% (1.04 g, 2.28 mmol); IR (KBr) 3390 (NH), 2950 cm^{-1} (*t*-Bu); ^{1}NMR ($CDCl_3$) δ 1.61 (s, 9 H), 5.46 (s, 1 H), 6.76−7.83 (m, 16 H). Anal. Calcd for $C_{28}H_{26}N_2O_2S$: C, 73.98; H, 5.76; N, 6.16. Found: C, 74.21; H, 5.82; N, 6.44.

***N*-[(4-Nitrophenyl)thio]-2-*tert*-butyl-4,6-diphenylaniline (6b):** brilliant yellow plates (ethanol); mp 158−160 °C; yield 45% (1.36 g, 2.99 mmol); IR (KBr) 3400 (NH), 2950 cm^{-1} (*t*-Bu); ^{1}H NMR ($CDCl_3$) δ 1.60 (s, 9 H), 5.41 (s, 1 H), 7.03 (d, J = 8.8 Hz, 2 H), 6.84−7.60 (m, 12 H), 7.91 (d, J = 8.8 Hz, 2H). Anal. Calcd for $C_{28}H_{26}N_2O_2S$: C, 73.98; H, 5.76; N, 6.16. Found: C, 74.05; H, 5.87; N, 6.40.

***N*-[(2,4-Dichlorophenyl)thio]-2-*tert*-butyl-4,6-diphenylaniline (6c):** colorless prisms (ethanol); mp 154−156 °C; yield 18% (0.58 g, 1.21 mmol); IR (KBr) 3380 (NH), 2950 cm^{-1} (*t*-Bu); ^{1}H NMR ($CDCl_3$) δ 1.59 (s, 9 H), 5.28 (s, 1 H), 6.93−7.58 (m, 15 H). Anal. Calcd for $C_{28}H_{25}Cl_2NS$: C, 70.23; H, 5.27; N, 2.93. Found: C, 70.36; H, 5.39; N, 3.18.

***N*-[(3,5-Dichlorophenyl)thio]-2-*tert*-butyl-4,6-diphenylaniline (6d):** light green plates (ethanol); mp 143−145 °C; yield 26% (0.82 g, 1.71 mmol); IR (KBr) 3400 (NH), 2950 cm^{-1} (*t*-Bu); ^{1}H NMR ($CDCl_3$) δ 1.58 (s, 9 H), 5.39 (s, 1 H), 6.74−7.57 (m, 15 H). Anal. Calcd for $C_{28}H_{25}Cl_2NS$: C, 70.23; H, 5.27; N, 2.93. Found: C, 70.44; H, 5.40; N, 3.22.

***N*-[(3-Nitrophenyl)thio]-2-*tert*-butyl-4,6-bis(4-chlorophenyl)aniline (6e):** light green prisms (ethanol); mp 132−134 °C; yield 23% (0.80 g, 1.53 mmol); IR (KBr) 3380 (NH), 2950 cm^{-1} (*t*-Bu); ^{1}H NMR ($CDCl_3$) δ 1.60 (s, 9 H), 5.53 (s, 1 H), 6.84−7.94 (m, 14 H). Anal. Calcd for $C_{28}H_{24}Cl_2N_2O_2S$: C, 64.24; H, 4.62; N, 5.35. Found: C, 64.37; H, 4.64; N, 5.34.

***N*-[(4-Nitrophenyl)thio]-2-*tert*-butyl-4,6-bis(4-chlorophenyl)aniline (6f):** yellow needles (ethanol); mp 171−173 °C; yield 50% (1.74 g, 3.32 mmol); IR (KBr) 3400 (NH), 2950 cm^{-1} (*t*-Bu); ^{1}H NMR ($CDCl_3$) δ 1.60 (s, 9 H), 5.47 (s, 1 H), 6.90 (d, J = 8.5 Hz, 2 H), 7.02 (d, J = 9.0 Hz, 2 H), 7.14 (d, J = 9.0 Hz, 2 H), 7.21 (d, J = 2.2 Hz, 1 H), 7.38 (d, J = 8.5 Hz, 2 H), 7.48 (d, J = 8.5 Hz, 2 H), 7.55 (d = 2.2 Hz, 1 H), 7.98 (d, J = 8.5 Hz, 2 H). Anal. Calcd for $C_{28}H_{24}Cl_2N_2O_2S$: C, 64.24; H, 4.62; N, 5.35. Found: C, 64.40; H, 4.70; N, 5.36.

***N*-[(2,4-Dichlorophenyl)thio]-2-*tert*-butyl-4,6-bis(4-chlorophenyl)aniline (6g):** colorless prisms (ethanol); mp 152−153 °C; yield 16% (0.57 g, 1.04 mmol); IR (KBr) 3420 (NH), 2950 cm^{-1} (*t*-Bu); ^{1}H NMR ($CDCl_3$) δ 1.58 (s, 9 H), 5.31 (s, 1 H), 6.94−7.53 (m, 13 H). Anal. Calcd for $C_{28}H_{23}Cl_4NS$: C, 61.44; H, 4.23; N, 2.56. Found: C, 61.73; H, 4.25; N, 2.61.

***N*-[(3-Nitrophenyl)thio]-4-*tert*-butyl-2,6-diphenylaniline (7a):** brilliant yellow plates (ethanol); mp 162−163 °C; yield 36% (1.10 g, 2.42 mmol); IR (KBr) 3300 (NH), 2950 cm^{-1} (*t*-Bu); ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 9 H), 5.27 (s, 1 H), 7.03−7.81 (m, 16 H). Anal. Calcd for $C_{28}H_{26}N_2O_2S$: C, 73.98; H, 5.77; N, 6.16. Found: C, 73.71; H, 5.73; N, 6.32.

***N*-[(4-Nitrophenyl)thio]-4-*tert*-butyl-2,6-diphenylaniline (7b):** brilliant yellow plates (ethanol); mp 146−148 °C; yield 43% (1.29 g, 2.84 mmol); IR (KBr) 3300 (NH), 2950 cm^{-1} (*t*-Bu); ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 9 H), 5.22 (s, 1 H), 6.85 (d, J = 8.8 Hz, 2 H), 7.21−7.42 (m, 12 H), 7.85 (d, J = 8.8 Hz, 2 H). Anal. Calcd for $C_{28}H_{26}N_2O_2S$: C, 73.98; H, 5.77; N, 6.16. Found: C, 74.24; H, 5.99; N, 6.26.

***N*-[(2,4-Dichlorophenyl)thio]-4-*tert*-butyl-2,6-diphenylaniline (7c):** colorless needles (ethanol); mp 131−132 °C; yield 30% (0.96 g, 2.01 mmol); IR (KBr) 3300 (NH), 2950 cm^{-1} (*t*-Bu); ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 9 H), 5.10 (s, 1 H), 6.87 (d, J = 8.3 Hz, 1 H), 6.92 (dd, J = 8.3 and 1.9 Hz, 1 H), 7.04 (d, J = 1.9 Hz, 1 H), 7.18 (s, 2 H), 7.23−7.39 (m, 10 H). Anal. Calcd for $C_{28}H_{25}Cl_2NS$: C, 70.28; H, 5.27; N, 2.93. Found: C, 70.14; H, 5.38; N, 2.99.

***N*-[(3,5-Dichlorophenyl)thio]-4-*tert*-butyl-2,6-diphenylaniline (7d):** colorless prisms (ethanol); mp 122−123 °C; yield 25% (0.80 g, 1.64 mmol); IR (KBr) 3330 (NH), 2950 cm^{-1} (*t*-Bu); ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 9 H), 5.23 (s, 1 H), 6.61 (d, J = 1.5 Hz, 2 H), 6.94 (t, J = 1.5 Hz, 1 H), 7.19 (s, 2 H), 7.25−7.40 (m, 10 H). Anal. Calcd for $C_{28}H_{25}Cl_2NS$: C, 70.28; H, 5.27; N, 2.93. Found: C, 70.05; H, 5.43; N, 3.16.

***N*-[(4-Chlorophenyl)thio]-4-*tert*-butyl-2,6-diphenylaniline (7e):** light green needles (ethanol); mp 103−104 °C; yield 16% (0.460 g, 1.04 mmol); IR ((KBr) 3280 (NH), 2950 cm^{-1} (*t*-Bu); ^{1}H NMR ($CDCl_3$) δ 1.31 (s, 9 H), 5.27 (s, 1 H), 6.69 (d, J = 8.5 Hz, 2 H), 7.00 (d, J = 8.5 Hz, 2 H), 7.17 (s, 2 H), 7.25−7.37 (m, 10 H). Anal. Calcd for $C_{28}H_{26}ClNS$: C, 75.74; H, 5.90; N, 3.16. Found: C, 75.51; H, 6.02; N, 2.92.

***N*-[(4-Bromophenyl)thio]-4-*tert*-butyl-2,6-diphenylaniline (7f):** light green needles (ethanol); mp 126−127 °C; yield 11% (0.37 g, 0.76 mmol); IR (KBr) 3280 (NH), 2950 cm^{-1} (*t*-Bu); ^{1}H NMR ($CDCl_3$) δ 1.31 (s, 9 H), 5.27 (s, 1 H), 6.63 (d, J = 8.3 Hz, 2 H), 7.14 (d, J = 8.3 Hz, 2 H), 7.17 (s, 2 H), 7.29−7.37 (m, 10 H). Anal. Calcd for $C_{28}H_{26}BrNS$: C, 68.84; H, 5.37; N, 2.87. Found: C, 68.65; H, 5.43; N, 2.78.

***N*-[(3-Nitrophenyl)thio]-4-*tert*-butyl-2,6-bis(4-chlorophenyl)aniline (7g):** light greenish yellow needles (ethanol); mp 150−152 °C; yield 35% (1.22 g, 2.33 mmol); IR (KBr) 3320

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(17) Kühle, E. *Synthesis* **1970**, 561 and **1971**, 617.

(NH), 2950 cm^{-1} (*t*-Bu); ^1H NMR ($CDCl_3$) δ 1.31 (s, 9 H), 5.15 (s, 1 H), 7.06−7.92 (m, 14 H). Anal. Calcd for $C_{28}H_{24}Cl_2N_2O_2S$: C, 64.24; H, 4.62; N, 5.35. Found: C, 64.30; H, 4.67; N, 5.40.

***N*-[(4-Nitrophenyl)thio]-4-*tert*-butyl-2,6-bis(4-chlorophenyl)aniline (7h):** light yellow plates (ethanol−benzene); mp 189−191 °C; yield 72% (2.50 g, 4.78 mmol); IR (KBr) 3330 (NH), 2950 cm^{-1} (*t*-Bu); ^1H NMR ($CDCl_3$) δ 1.32 (s, 9 H), 5.10 (s, 1 H), 6.89 (d, J = 8.8 Hz, 2 H), 7.17 (s, 2 H), 7.26 (d, J = 8.3 Hz, 4 H), 7.30 (d, J = 8.3 Hz, 4 H), 7.93 (d, J = 8.8 Hz, 2 H). Anal. Calcd for $C_{28}H_{24}Cl_2N_2O_2S$: C, 64.24; H, 4.62; N, 5.35. Found: C, 64.33; H, 4.62; N, 5.37.

***N*-[(2,4-Dichlorophenyl)thio]-4-*tert*-butyl-2,6-bis(4-chlorophenyl)aniline (7i):** colorless needles (ethanol−benzene); mp 173−175 °C; yield 15% (0.53 g, 0.97 mmol); IR (KBr) 3320 (NH), 2950 cm^{-1} (*t*-Bu); ^1H NMR ($CDCl_3$) δ 1.31(s, 9 H), 4.95 (s, 1 H), 6.88 (d, J = 8.5 Hz, 1 H), 6.98 (dd, J = 8.5 and 2.2 Hz, 1 H), 7.12 (d, J = 2.2 Hz, 1 H), 7.14 (s, 2 H), 7.27 (s, 8 H). Anal. Calcd for $C_{28}H_{23}Cl_4NS$: C, 61.44; H, 4.24; N, 2.56. Found: 61.69; H, 4.29; N, 2.63.

***N*-[(3,5-Dichlorophenyl)thio]-4-*tert*-butyl-2,6-bis(4-chlorophenyl)aniline (7j):** light green needles (ethanol); mp 169−172 °C; yield 50% (1.81 g, 3.31 mmol); IR (KBr) 3280 (NH), 2950 cm^{-1} (*t*-Bu); ^1H NMR ($CDCl_3$) δ 1.31 (s, 9 H), 5.08 (s, 1 H), 6.64 (s, 1 H), 7.03 (s, 2 H), 7.15 (s, 2 H), 7.30 (d, J = 8.8 Hz, 4 H), 7.31 (d, J = 8.8 Hz, 4 H). Anal. Calcd for $C_{28}H_{23}Cl_4NS$: C, 61.44; H, 4.24; N, 2.56. Found: 61.61; H, 4.25; N, 2.69.

2-*tert*-Butyl-4,6-di(phenyl-d_5)aniline. By the same procedure as for 2-*tert*-butyl-4,6-diphenylaniline, 6.05 g (19.7 mmol) of 2-*tert*-butyl-4,6-dibromoaniline was treated with 7.50 g (59.1 mmol) of phenylboronic-d_5 acid in the presence of 2.73 g (2.36 mmol) of $(PPh_3)_4Pd$ and 16.7 g of Na_2CO_3 in a mixed solvent of 200 mL of benzene, 40 mL of ethanol, and 79 mL of water at the reflux temperature for 24 h under nitrogen. After the usual workup, the reaction mixture was chromatographed on silica gel with 5:1 benzene−hexane as eluant. Crystallization from hexane gave colorless needles with mp 98−100 °C in 80% yield (4.88 g, 15.7 mmol): IR (KBr) 3460 and 3360 (NH_2), 2950 (*t*-Bu), 2250 cm^{-1} (CD); ^1H NMR ($CDCl_3$) δ 1.52 (s, 9 H), 4.02 (s, 2 H), 7.26 (d, J = 2.2 Hz, 1H), 7.53 (d, J = 2.2 Hz, 1 H). Anal. Calcd for $C_{22}H_{13}D_{10}N$: C, 84.84; H, 7.44; N, 4.50. Found: C, 84.75; H, 7.68; N, 4.53.

4-*tert*-Butyl-2,6-di(phenyl-d_5)aniline. By the same procedure as for 4-*tert*-butyl-2,6-diphenylaniline, 4.61 g (15.0 mmol) of 4-*tert*-butyl-2,6-dibromoaniline was treated with 5.08 g (45 mmol) of phenylboronic-d_5 acid in the presence of 2.73 g (1.80 mmol) of $(PPh_3)_4Pd$ and 12.7 g of Na_2CO_3 in a benzene (150)−ethanol (30)−water (60 mL) mixed solvent at the reflux temperature for 24 h under nitrogen. After the usual workup, the reaction mixture was chromatographed on silica gel with 5:1 benzene−hexane as eluant. Crystallization from hexane gave colorless needles with mp 90−93 °C in 83% yield (3.88 g, 12.5 mmol): IR (KBr) 3410 and 3310 (NH_2), 2950 (*t*-Bu), 2250 cm^{-1} (CD); ^1H NMR ($CDCl_3$) δ 1.33 (s, 9 H), 3.7 (br s, 2 H), 7.16 (s, 2 H). Anal. Calcd for $C_{22}H_{13}D_{10}N$: C, 84.84; H, 7.44; N, 4.50. Found: C, 84.70; H, 7.57; N, 4.78.

General Procedure for Preparation of *N*-(Arylthio)-2-*tert*-butyl-4,6-di(phenyl-d_5)anilines (10) and *N*-(Arylthio)-4-*tert*-butyl-2,6-di(phenyl-d_5)anilines (11). Precursors **10** and **11** were prepared by the same procedure as for **6** and **7**. Thus, a solution of 4.82 mmol of arenesulfenyl chloride in 30 mL of dry ether was added to a stirred solution of 1.00 g (3.21 mmol) of 2-*tert*-butyl-4,6-di(phenyl-d_5)aniline [or 4-*tert*-butyl-2,6-di(phenyl-d_5)aniline] and 0.73 g (7.2 mmol) of triethylamine in 100 mL of dry ether at 0 °C. After the addition was completed, the mixture (sometime colored) was continued to stir for 2 h at 0 °C. After filtration, the filtrate was evaporated under reduced pressure, and the residue was chromatographed on alumina using 1:1 (**10a**, **11a**), 1:3 (**11b**, **11c**), or 1:5 benzene−hexane (**10b**) as eluant to give a pure solid or a solid containing small amounts of diaryl disulfide and/or the starting aniline. Crystallization from ethanol gave pure compounds.

***N*-[(4-Nitrophenyl)thio]-2-*tert*-butyl-4,6-di(phenyl-d_5)aniline (10a):** brilliant yellow plates; mp 158−160 °C; yield 24% (0.36 g, 0.77 mmol); IR (KBr) 3350 (NH), 2950 (*t*-Bu), 2240 cm^{-1} (CD); ^1H NMR ($CDCl_3$) δ 1.60 (s, 9 H), 5.41 (s, 1 H), 7.03 (d, J = 9.0 Hz, 2 H), 7.30 (d, J = 2.2 Hz, 1 H), 7.60 (d, J = 2.2 Hz, 1 H), 7.91 (d, J = 9.0 Hz, 2 H). Anal. Calcd for $C_{28}H_{16}D_{10}N_2O_2S$: C, 72.38; H, 5.64; N, 6.03. Found: C, 72.60; H, 5.85; N, 6.04.

***N*-[(3,5-Dichlorophenyl)thio]-2-*tert*-butyl-4,6-di(phenyl-d_5)aniline (10b):** light green plates; mp 137 −138 °C; yield 34% (0.53 g, 1.08 mmol); IR (KBr) 3420 (NH), 2950 (*t*-Bu), 2250 cm^{-1} (CD); ^1H NMR ($CDCl_3$) δ 1.58 (s, 9 H), 5.39 (s, 1 H), 6.74 (s, 2 H), 6.95 (s, 1 H), 7.29 (s, 1 H), 7.57 (s, 1 H). Anal. Calcd for $C_{28}H_{15}D_{10}NSCl_2$: C, 68.84; H, 5.16; N, 2.87. Found: C, 68.66; H, 5.29; N, 2.82.

***N*-[(4-Nitrophenyl)thio]-4-*tert*-butyl-2,6-di(phenyl-d_5)aniline (11a):** brilliant yellow plates; mp 142−143 °C; yield 75% (1.11 g, 2.40 mmol); IR (KBr) 3300 (NH), 2950 (*t*-Bu); 2250 cm^{-1} (CD); ^1H NMR ($CDCl_3$) δ 1.32 (s, 9 H), 5.23 (s, 1 H), 6.85 (d, J = 8.8 Hz, 2 H), 7.21 (s, 2 H), 7.85 (d, J = 8.8 Hz, 2 H). Anal. Calcd for $C_{28}H_{16}D_{10}N_2O_2S$: C, 72.38; H, 5.64; N, 6.03. Found: C, 72.20; H, 5.78; N, 5.96.

***N*-[(4-Bromophenyl)thio]-4-*tert*-butyl-2,6-di(phenyl-d_5)aniline (11b):** light green needles; mp 118−121 °C; yield 23% (0.37 g, 0.73 mmol); IR (KBr) 3270 (NH), 2950 (*t*-Bu), 2250 cm^{-1} (CD); ^1H NMR ($CDCl_3$) δ 1.31 (s, 9 H), 5.27 (s, 1 H), 6.62 (d, J = 8.3 Hz, 2 H), 7.14 (d, J = 8.3 Hz, 2 H), 7.17 (s, 2 H). Anal. Calcd for $C_{28}H_{16}BrD_{10}NS$: C, 67.46; H, 5.26; N, 2.81. Found: C, 67.79; H, 5.17; N, 2.74.

***N*-[(4-Bromophenyl-d_5)thio]-4-*tert*-butyl-2,6-di(phenyl-d_5)aniline (11c):** light green needles; mp 119−122 °C; yield 16% (0.26 g, 0.51 mmol); IR (KBr) 3300 (NH), 2950 (*t*-Bu), 2280 cm^{-1} (CD); ^1H NMR ($CDCl_3$) δ 1.31 (s, 9 H), 5.26 (s, 1 H), 7.17 (s, 2 H). Anal. Calcd for $C_{28}H_{12}BrD_{14}NS$: C, 66.92; H, 5.22; N, 2.79. Found: C, 66.91; H, 5.31; N, 2.72.

Isolation of Aminyl Radicals. Precursor **5** or **6** (100 mg) was dissolved in 20 mL of benzene with stirring. After 1.0 g of K_2CO_3 was added, PbO_2 (1.0 g) was added to the vigorously stirred benzene solution in some portions during 2 min. After completion of the addition, stirring was continued for an additional 0.5 min, and the strongly colored mixture was filtered. The solvent was removed by freeze-drying, and the resulting strongly colored crystalline residue was recrystallized from hexane (**2b**, **2j**), ethanol (**1b**, **1f**), or hexane−ethyl acetate (**2h**).

***N*-[(4-Nitrophenyl)thio]-2-*tert*-butyl-4,6-diphenylphenylaminyl (1b):** black needles; mp 139−141 °C; yield 56% (56.1 mg, 0.12 mmol); IR (KBr) 2950, 1590, 1570, 1510, 1440, 1330, 1260, 1215, 1180, 1110, 1070, 1050, 1020, 890, 870, 860, 820, 790, 760, 740, 710, 700, 680, 650 cm^{-1}. Anal. Calcd for $C_{28}H_{25}N_2O_2S$: C, 74.14; H, 5.56; N, 6.18. Found: C, 74.20; H, 5.81; N, 6.12.

***N*-[(4-Nitrophenyl)thio]-2-*tert*-butyl-4,6-bis(4-chlorophenyl)phenylaminyl (1f):** black needles; mp 161−163 °C; yield 48% (48 mg, 0.091 mmol); IR (KBr) 2950, 1590, 1580, 1510, 1485, 1330, 1170, 1090, 1070, 1010, 850, 840, 820, 740 cm^{-1}. Anal. Calcd for $C_{28}H_{23}Cl_2N_2O_2S$: C, 64.37; H, 4.44; N, 5.36. Found: C, 64.40 ; H, 4.43; N, 5.33.

***N*-[(4-Nitrophenyl)thio]-4-*tert*-butyl-2,6-diphenylphenylaminyl (2b):** black prisms; mp 140−142 °C; yield 43% (43 mg, 0.094 mmol); IR (KBr) 2950, 1570, 1510, 1330, 1240, 1105, 1075, 890, 855, 785, 775, 755, 740, 705 cm^{-1}. Anal. Calcd for $C_{28}H_{25}N_2O_2S$: C, 74.14; H, 5.56; N, 6.18. Found: C, 73.87; H, 5.41; N, 6.23.

***N*-[(4-Nitrophenyl)thio]-4-*tert*-butyl-2,6-bis(4-chlorophenyl)phenylaminyl (2h):** black prisms; mp 123−125 °C; yield 47% (47 mg, 0.091 mmol); IR (KBr): 2950, 1590, 1570, 1520, 1490, 1340, 1250, 1110, 1090, 1020, 860, 830, 740 cm^{-1}. Anal. Calcd for $C_{28}H_{23}Cl_2N_2O_2S$: C, 64.37; H, 4.44; N, 5.36. Found: C, 64.62; H, 4.53; N, 5.46.

***N*-[(3,5-Dichlorophenyl)thio]-4-*tert*-butyl-2,6-bis(4-chlorophenyl)phenylaminyl (2j):** dark brown needles; mp 138−139 °C; yield 33% (33 mg, 0.060 mmol); IR (KBr) 2950, 1560, 1490, 1460, 1400, 1240, 1135, 1095, 1000, 830, 800, 735, 720, 660 cm^{-1}. Anal. Calcd for $C_{28}H_{22}Cl_4NS$: C, 61.55; H, 4.06; N, 2.56. Found: C, 61.80; H, 4.06; N, 2.88.

ESR Measurements. ESR spectra were measured on a JEOL JES-ME-3X or Bruker ESP300 spectrometer operating

at X-band with 100 kHz field modulation. Hyperfine splitting constants and *g* values were determined by the simulutaneous measurements with a dilute Fremy's salt in a dilute K_2CO_3 aqueous solution (a_N = 1.309 mT, g = 2.0057) as reference. Estimated accuracies: ±0.01 mT for a_N and a_H, ±0.02 mT for $a33_S$ and $a13_C$, and ±0.0001 for g.

^{1}H ENDOR Measurements. ^{1}H ENDOR measurements were carried out at −75 °C on a Bruker (300/350) ENDOR spectrometer equipped with a TM_{011} mode microwave cavity operating at X-band using toluene as solvent.

X-ray Crystallographic Analysis of 1b.[21] A black needle crystal of $C_{28}H_{25}N_2O_2S$ (M = 453.58) having approximate dimensions of 0.20 × 0.20 × 0.20 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Cu *K*α radiation (λ = 1.54178 Å). Monoclinic, space group $P2_1$, a = 14.095(5), b = 5.855(4), c = 14.124(3) Å, β = 90.92(2)°, V = 1165.5(8) Å^3, Z = 2, D_c = 1.29 g cm^{-3}.

The data were collected at a temperature of 23 ± 1°C using the ω - 2θ scan technique to a 2θ value of 113.6°. The linear absorption coefficient, μ, for Cu *K*α radiation is 14.5 cm^{-1}. An empirical absorption correction using the program DIFABS[18] was applied which resulted in transmission factors ranging from 0.90 to 1.10.

The structure was solved by direct methods[19] and expanded using Fourier techniques.[20] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. Of the 1838 reflections collected, 1658 reflections with $I > 3.00\sigma(I)$ were observed. The final cycle of full-matrix least-squares refinement was based on the observed reflections and 397 variable parameters and converged with the unweighted and weighted agreement factors of R = 0.035 and R_w = 0.034.

X-ray Crystallographic Analysis of 2b.[21] A black prismatic crystal of $C_{28}H_{25}N_2O_2S$ (M = 453.58) having approximate dimensions of 0.50 × 0.80 × 0.80 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Cu *K*α radiation (λ = 1.54178 Å). Monoclinic, space group $P2_1/n$, a = 11.434-(2), b = 13.453(2), c = 15.860(2), β = 101.46(1)°, V = 2390.9-(6) Å, Z = 4, D_c = 1.260 g cm^{-3}.

The data were collected at a temperature of 20 ± 1 °C using the ω - 2θ scan technique to a 2θ value of 120.2°. The linear absorption coefficient, μ, for Cu *K*α radiation is 14.2 cm^{-1}. An empirical absorption correction using the program DIFABS[18] was applied which resulted in transmission factors ranging from 0.82 to 1.26.

The structure was solved by direct methods[19] and expanded using Fourier techniques.[20] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. Of the 3951 reflections collected, 3217 reflections with $I > 3.00\sigma(I)$ were observed. The final cycle of full-matrix least-squares refinement was based on the observed reflections and 398 variable parameters and converged with the unweighted and weighted agreement factors of R = 0.054 and R_w = 0.085.

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(21) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.