Electron Spin Resonance Spectra of Sulfinamidyl Radicals and a Comparison of Hyperfine Splitting Constants with Sulfenamidyl and Sulfonamidyl Radicals[1)]

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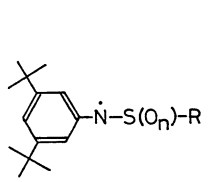
An ESR spectroscopic study of *N*-arylsulfinyl- and *N*-alkylsulfinyl-3,5-di-*t*-butylphenylaminyls (**2**) is described. The sulfinamidyls **2**, generated by the reaction of the corresponding sulfinamides (**7**) with di-*t*-butyl diperoxyoxalate (DBPO) in benzene at 21 or 40 °C, give hyperfine splitting (hfs) constants which indicate that the unpaired electron is slightly delocalized onto the sulfinyl group. A comparison of the hfs constants for **2** with those for structurally related sulfenamidyl and sulfonamidyl radicals indicates that the abilities of -SR, -S(O)R, and -S(O$_2$)R to delocalize the unpaired electron are in the order -SR>-S(O)R>-(O$_2$)R. The reaction of **7** with DBPO has been examined on the basis of product analyses. The mechanism accounting for the formation of the isolated products is briefly discussed.

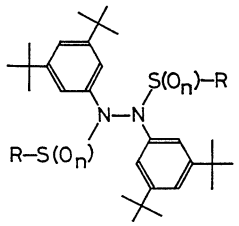
Since sulfenamidyls (RṄSR′), sulfinamidyls [RṄS(O)R′], and sulfonamidyls [RṄS(O$_2$)R′] are structurally close to each other, it is of considerable interest to compare their spin density distributions or stabilities. Sulfenamidyls, which are the lowest in the oxidation state of the sulfur, and sulfonamidyls, which are the highest in the oxidation state of the sulfur, have already been widely investigated by means of ESR spectroscopy by our and other groups.[2,3)]

The ESR studies of sulfenamidyls have shown that in the radicals the unpaired electron is substantially delocalized from the nitrogen to the sulfur,[4)] and that this conjugative delocalization brings about a great stability to sulfenamidyls. The typical persistent sulfenamidyls prepared are *N*-arylthio-3,5-di-*t*-butylphenylaminyls[5)] (**1**) and *N*-(*p*-nitrophenylthio)-2,4,6-tri-*t*-butylphenylaminyl.[6)] The former radicals persist for one month, even in the presence of atmospheric oxygen, and can be isolated as hydrazine-like dimers (**4**) which dissociate, upon dissolution, into **1**, even at room temperature (the ΔH° and ΔS° values for the **4**⇄2 **1** equlibrium in benzene are 55.6—57.7 kJ mol^{-1} and 121—122 J mol^{-1} K^{-1}, respectively).

On the other hand, an ESR study of the sulfonamidyls **3** has shown that in **3** there is no or little delocalization of the unpaired electron onto the sulfonyl group. The dimer (**6**) of **3**, therefore, gave a high ΔH° value



1: n=0 2: n=1 3: n=2



4: n=0 5: n=1 6: n=2

of 131 kJ mol^{-1} for the **6**⇄2 **3** equilibrium in benzene (the ΔS° value, 141 J mol^{-1} K^{-1}).

In an extension of the above ESR studies, we investigated the sulfinamidyls **2** by means of ESR spectroscopy. In contrast to a large body of ESR studies on sulfenamidyls and sulfonamidyls, there have appeared only two brief ESR studies on sulfinamidyls in the literature.[8)] Herein, we wish to report on our ESR study of the sulfinamidyls **2**.

Results and Discussion

Sulfinamidyls **2a—g** were generated in the cavity of an ESR instrument by the reaction of the corresponding sulfinamides (**7a—g**) with di-*t*-butyl diperoxyoxalate (DBPO) in benzene at 21 or 40 °C. DBPO is known to decompose, even at room temperature, to

Table 1. ESR Parameteters for **2**[a,b)]

Sulfinamidyl radical	Temp °C	a_N	$a_{o\text{-}H}$[c)]	$a_{p\text{-}H}$[d)]	a_{other}	g
		mT				
2a	21	0.817	0.488	0.646		2.0035
2b	21	0.818	0.486	0.644		2.0035
2c	21	0.818	0.487	0.644		2.0035
2d	21	0.813	0.482	0.643		2.0034
2e	40	0.816	0.489	0.638	0.085 (3 H)[e)]	2.0034

a) Hyperfine splitting constants are determined by the computer-simulation method. b) Solvent, benzene. c) Due to the ortho protons (2 H) of the anilino group. d) Due to the para proton (1 H) of the anilino group. e) Due to the methyl protons (3 H).

give two *t*-BuO· radicals with the evolution of CO_2.[9] The hyperfine splitting (hfs) constants and *g* values for **2** are summarized in Table 1, and typical ESR spectra are illustrated in Figs. 1 and 2.

All of the ESR spectra recorded were very weak, indicating tnat **2** is a transient radical. As found in Fig. 1, the ESR spectrum is split into a 1 : 1 : 1 triplet of 1 : 1 doublets of 1 : 2 : 1 triplets. The 1 : 1 : 1 triplet splitting is due to an interaction with nitrogen, while the 1 : 1 doublet and 1 : 2 : 1 triplet splittings are due to

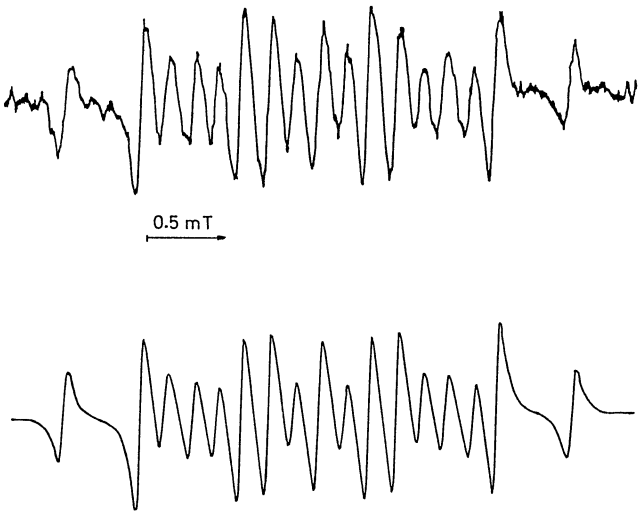


Fig. 1. ESR spectrum of **2c** in benzene recorded at 21 °C (upper), and the spectrum simulated by using the hfs constants shown in Table 1 (bottom).

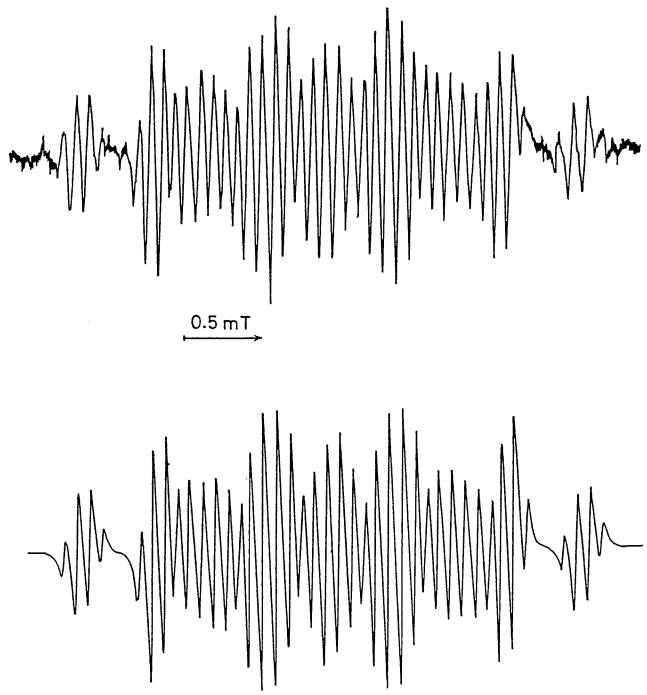
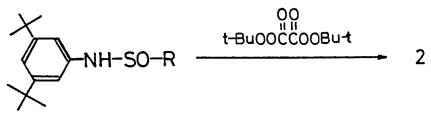


Fig. 2. ESR spectrum of **2e** in benzene recorded at 40 °C (upper), and the spectrum simulated by using the hfs constants shown in Table 1 (bottom).



7

a: R=Ph e: R=Me

b: R=4-MeC_6H_4 f: R=Et

c: R=4-t-BuC_6H_4 h: R=i-Pr

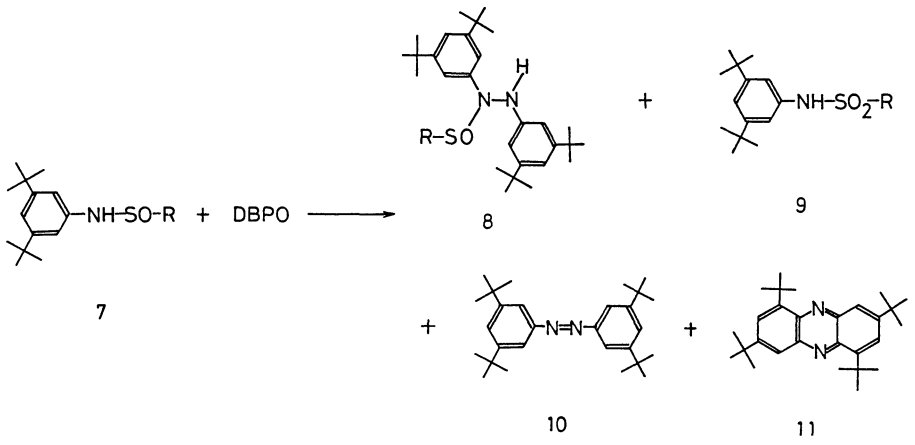
d: R=4-ClC_6H_4

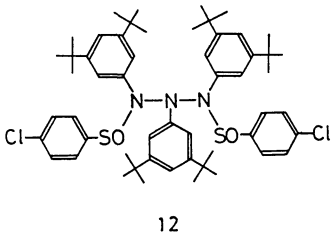
interactions with the para and ortho protons of the anilino group. However, no splittings due to the aromatic protons of -S(O)Ar were detectable. The sulfinamidyls **2a**, **2b**, and **2c** also gave almost the same ESR spectra.

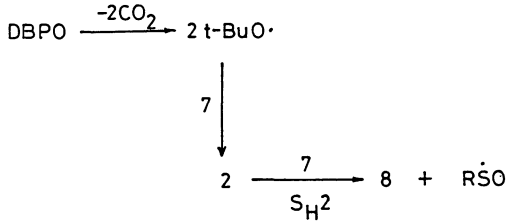
The sulfinamidyl **2e** gave a more complex ESR spectrum than those of **2a—d**, as found in Fig. 2, since the splittings due to the methyl protons were further added. On the other hand, the ESR spectra of **2f** and **2g** were much weaker and more complex than that of **2e**. In those spectra, the splittings due to the δ protons may appear, in addition to the splittings due to the nitrogen, ortho and para protons of the anilino group, and γ protons. Although attemps were made to analyze the spectra by a computer simulation method, satisfactory results were not obtained owing to the low S/N ratio of the spectra.

Reaction of 7 with DBPO. As previously reported, the dimers **6** can be isolated from the reaction of the corresponding sulfonamides with DBPO.[3] Since the sulfinamidyls **2** have been generated by the reaction of **7** with DBPO, the successful isolation of **6** prompted us to analyze the products from the reaction of **7** with DBPO.

The reaction of **7** with DBPO was carried out by stirring a mixture of **7** and DBPO in benzene at room temperature for one day under nitrogen. The products isolated from the reaction of **7d** with DBPO were **8d** (27%), **9d** (25%), **10** (9%), and **11** (0.7%),[10] while those isolated from the reaction of **7e** with DBPO were **8e** (31%), **9e** (16%), **10** (12%), and **11** (1%).[10] Although the expected dimer **5** could not be isolated from any reaction mixtures, the azo compound **10**, which is expected to be derived from **5**, was isolated in 9—12% yields. For the formation of **10**, however, there still remains another possibility; namely, hydrogen-atom abstraction from **8** by *t*-BuO· radicals, followed by the loss of a RṠO radical. To check this possibility, the reaction of **8d** with DBPO was carried out by stirring a mixture of **8d** and 1. 2 equiv of DBPO in benzene at room temperature under nitrogen. The major isolated product was **12** (65%), while **10** was shown by TLC analysis of the reaction mixture to be formed only slightly. Consequently, the above possibility







Scheme 1.

was unequivocally excluded. The dimers **5** may be much more thermally labile than anticipated.

Although the reaction mechanism for the formation of **8** is still unclear, it might be formed by a bimolecular homolytic substitution (S_H2) process at the nitrogen of **7**,[11] as shown in Scheme 1. Compound **8** was expected to give **5** by a reaction with sulfinyl chlorides in the presence of Et_3N; however, no reaction between **8** and the sulfinyl chlorides occurred.

Comparison of Hfs Constants. An estimate of the spin density withdrawn by -SR, -S(O)R, and -S(O_2)R has been discussed for MeĊHS(O_n)R radicals[12] (n=0, 1, 2) and p-substituted benzyl and phenoxyl radicals.[13,14] It was reported that in MeĊHS(O_n)R radicals, -S(O_2)Et was wholly uninfluenced upon removing the spin, while -S(O)Et and -SEt removed ca. 6 and 22% of the spin density from the trivalent carbon, respectively.

For **1**, **2**, and **3**, the extents of the spin density withdrawn by -S(O_n)R can be estimated from the magnitudes of the hfs constants due to the protons in R. As can be seen from Table 2, the sulfenamidyls **1** give relatively large splittings due to the aromatic protons of -SPh (0.027—0.083 mT) and due to the γ protons (-SCH_2-) (0.259 mT), indicating that a considerable amount of the spin is delocalized onto -SR. For **2**, on the other hand, only small splittings (0.085 mT) due to the methyl protons were found;[15] for **3**, splittings due to R protons were no longer detectable.

The extents of the spin density withdrawn by -S(O_n)R can also be estimated from the magnitudes of

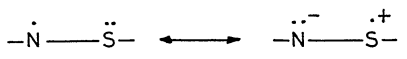
Table 2. Comparison of the Hyperfine Splitting Constants for ArṄSR, ArṄS(O)R, and ArṄS(O_2)R

Radical	a_N	$a_{o\text{-}H}$[b]	$a_{p\text{-}H}$[c]	a_{other}			Ref.
	mT						
ArṄSPh	0.953	0.371	0.422	0.076[d]	0.027[e]	0.083[f]	5
ArṄSCH$_2$CH$_2$CH$_2$CH$_3$	0.975	0.373	0.421		0.259[g]		16
ArṄS(O)Ph	0.817	0.488	0.646				This work
ArṄS(O)CH$_3$	0.816	0.489	0.638		0.085[h]		This work
ArṄS(O_2)Ph	0.761	0.563	0.820				3
ArṄS(O_2)CH$_3$	0.740	0.559	0.806				3

a) Ar: 3,5-Di-*t*-butylphenyl. b) Due to the ortho protons of the anilino group. c) Due to the para proton of the anilino group. d) Due to the ortho protons of -SPh. e) Due to the meta protons of -SPh. f) Due to the para proton of -SPh. g) Due to the γ protons (-SCH_2-) h) Due to the methyl protons.

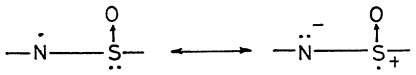
the hfs constants due to the aromatic protons of the anilino groups. As shown in Table 2, the aromatic proton hfs constants reduce in the order **3**>**2**>**1**, indicating that the extents of the spin density withdrawn by -S(O_n)R increase in the order -S(O_2)R<-S(O)R< -SR, in agreement with the above results obtained from the magnitudes of the proton hfs constants due to R.

A sulfenyl sulfur accommodates a lone pair of electrons in the 3p orbital of a high energy level. An effective conjugative delocalization of the unpaired electron from the nitrogen to the sulfur is therefore possible.[18] Although a sulfinyl sulfur still has one



A B

lone pair of electrons, they are accommodated in the sp^3 hybrid orbital of a low energy level and the electonegative oxygen binds to the sulfur. Accordingly, the dipolar canonical structure **D** contributes less to



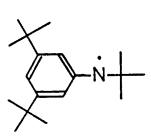
C D

the resonance hybrid of **2** than does the corresponding dipolar canonical structure **B** to the hybrid of **1**. A conjugative delocalization of the unpaired electron from the nitrogen to the sulfur is, therefore, less important in **2** than in **1**. On the other hand, a sulfonyl sulfur no longer has a lone pair of electrons. Conjugative delocalization of the unpaired electron, such as **A**⟷**B** or **C**⟷**D**, therefore, can not be drawn.

In general, a_N values are correlated with the π-spin density on nitrogen by Eq. 1, where Q_N is a constant and ρ_N^π is the π-spin density on nitrogen. The Q_N value is approximately constant for the

$$a_N = Q_N \rho_N^\pi \quad (1)$$

radicals of analogous structures, but no longer constant when the rigand electronegativity or rigand bulkiness is largely different.[17] For example, although the aromatic proton hfs constants for **3** and **13** are very similar to each other, and the abilities of -S(O_2)R and *t*-Bu to delocalize the unpaired electron



13

a_N: 0.944; $a_{o\text{-}H}$: 0.565; $a_{p\text{-}H}$: 0.713 mT

are both negligibly small, there is a relatively large difference (0.183—0.204 mT) between the magitudes of their a_N values. A similar situation seems also to occur in **1**, **2**, and **3**. That is, the order in the magnitudes of the a_N values (**1**>**2**>**3**) does not necessary represent the order in the spin densities on the nitrogens. Taking into account the extents of the spin densities withdrawn by -SR, -S(O)R, and -S(O_2)R, the spin densities on the nitrogens seem, like those on the anilino benzene rings, to decrease in the order **3**>**2**>**1** rather than **1**>**2**>**3**. If this is true, the Q_N values should increase in the order **3**>**2**>**1**. To discuss the spin density distributions in these radicals in more detail, molecular orbital calculations are now being performed.

In summary, we describe an ESR study of the sulfinamidyls **2**. The very weak ESR signals of **2** indicate that **2** is a transient radical; the small or lack of splittings due to the protons of -S(O)R reveal only a slight delocalization of the unpaired electron onto the sulfinyl groups. A comparison of the hfs constants for **1**, **2**, and **3** indicates that the extents of the spin densities withdrawn by -SR, -S(O)R, and -S(O_2)R increase in the order -S(O_2)R<-S(O)R<-SR, in agreement with those reported for carbon radicals.

Experimental

Melting points were determined on a Yanagimoto micro melting apparatus and are uncorrected. IR spectra were run on a JASCO A-202 spectrophotometer and mass spectra were taken by direct insertion on a JEOL D-300 spectrometer. ^{1}H NMR spectra were recorded with a JEOL PS-100 spectrometer (100 MHz) and chemical shifts are expressed in ppm values (δ) using Me_4Si as an internal standard.

3,5-Di-*t*-butylaniline[19] and di-t-butyl diperoxyoxalate[9] (DBPO) were obtained by the reported methods. Methane-, ethane-, and 2-methylethanesulfinyl chlorides were prepared by passing Cl_2 through a solution of the corresponding alkyl disulfide and acetic anhydride and were purified by distillation.[20] Arenesulfinyl chlorides were prepared by passing Cl_2 through a solution of arenethiol and an equiv of acetic acid in dry $CHCl_3$ at 0 °C. After removing volatile materials (e.g., Cl_2 and MeCOCl) under reduced pressure, they were used in the following step without further purification.

General Procedure for Preparation of *N*-Arylsulfinyl- and *N*-Alkylsulfinyl-3,5-di-*t*-butylanilines (7). A solution of 10.3 mmol of a sulfinyl chloride in 20 ml of dry ether was added dropwise to a stirred solution of 2.00 g (9.74 mmol) of 3,5-di-*t*-butylaniline and 1.45 g (14.3 mmol) of triethylamine in 150 ml of dry ether at 0 °C. After completion of the addition, the mixture was stirred for 2 h at the same temperature, filtered, and evaporated under reduced pressure. The sulfinamides **2b—d** were purified by crystallization from hexane or benzene-hexane, while **7a** was purified by column chromatography [silica gel (Waka gel C-200), column size 35×30 cm, eluant 1:10 ethyl acetate-benzene] and subsequent crystallization from hexane. On the other hand, **7e—g** were purified by crystallization from hexane or benzene-hexane after the polar by-products were removed using

a short column (Merck aluminium oxide 90, eluant 1:1 ethyl acetate-hexane).

***N*-Phenylsulfinyl-3,5-di-*t*-butylaniline (7a):** Yield 2.06 g (6.25 mmol, 64/%); colorless prisms; mp 98—99 °C; IR (KBr) 3150 (NH), 2950—2850 (*t*-Bu), 1060 cm^{-1} (SO); ^1H NMR ($CDCl_3$) δ=1.26 (s, *t*-Bu, 18 H), 6.32 (br s, NH, 1 H), 6.88—7.81 (m, aromatic, 8 H). Found: C, 72.85; H, 8.35; N, 4.36 %. Calcd for $C_{20}H_{27}NOS$: C, 72.90; H, 8.26; N, 4.25%.

***N*-(*p*-Tolylsulfinyl)-3,5-di-*t*-butylaniline (7b):** Yield 1.59 g (4.63 mmol, 48%); colorless needles; mp 144—146 °C; IR (KBr) 3130 (NH), 2950—2850 (*t*-Bu), 1060 cm^{-1} (SO); ^1H NMR ($CDCl_3$) δ=1.28 (s, *t*-Bu, 18 H), 2.38 (s, Me, 3 H), 6.13 (br s, NH, 1 H), 6.89—7.71 (m, aromatic, 7 H). Found: C, 73.17; H, 8.13; N, 3.91%. Calcd for $C_{21}H_{29}NOS$: C, 73.42; H, 8.51; N, 4.08%.

***N*-(4-*t*-Butylphenylsulfinyl)-3,5-di-*t*-butylaniline (7c):** Yield 2.44 g (6.33 mmol, 65%), colorless needles; mp 141—143 °C; IR (KBr) 3150 (NH), 2950—2850 (*t*-Bu), 1060 cm^{-1} (SO); ^1H NMR ($CDCl_3$) δ=1.28 (s, *t*-Bu, 18 H) , 1.35 (s, *t*-Bu, 9 H) , 6.19 (br s, NH, 1 H), 6.87—7.77 (m, aromatic, 7 H). Found: C, 74.60; H, 8.87; N, 3.45%. Calcd for $C_{24}H_{35}NOS$: C, 74.75; H, 9.15; N, 3.63%.

***N*-(4-Chlorophenylsulfinyl)-3,5-di-*t*-butylaniline (7d):** Yield 1.90 g (5.22 mmol, 57%); colorless needles; mp 162—164 °C; IR (KBr) 3130 (NH), 2950—2850 (*t*-Bu), 1060 cm^{-1} (SO); ^1H NMR ($CDCl_3$) δ=1.28 (s, *t*-Bu, 18 H), 6.30 (br s, NH, 1 H), 6.90—7.79 (m, aromatic, 7 H). Found: C, 66.11; H, 7.21; N, 3.92%. Calcd for $C_{20}H_{26}ClNOS$: C, 66.00; H, 7.20; N, 3.85%.

***N*-Methylsulfinyl-3,5-di-*t*-butylaniline (7e):** Yield 1.53 g (5.70 mmol, 59%); colorless prisms ; mp 142—143 °C; IR (KBr) 3130 (NH) , 2950—2850 (*t*-Bu), 1050 cm^{-1} (SO); ^1H NMR ($CDCl_3$) δ=1.27 (s, *t*-Bu, 18 H), 2.81 (s, Me, 3 H), 6.88—7.06 (m, aromatic, 3 H), 7.90 (br s, NH, 1 H). Found: C, 67.53; H, 9.57; N, 4.94%. Calcd for $C_{15}H_{25}NOS$: C, 67.36; H, 9.42; N, 5.24%.

***N*-Ethylsulfinyl-3,5-di-*t*-butylaniline (7f):** Yield 0.94 g (3.33 mmol, 34%); colorless needles; mp 137—138 °C; IR (KBr) 3130 (NH), 2950—2850 (*t*-Bu), 1060 cm^{-1} (SO); ^1H NMR ($CDCl_3$) δ=1.27 (s, *t*-Bu, 18 H), 1.30 (t, J=8.0 Hz, $CH_2\underline{CH_3}$, 3H), 2.99 (q, J=8.0 Hz, $\underline{CH_2}CH_3$, 2 H), 6.88—7.06 (m, aromatic, 3 H), 7.01 (br s, NH, 1 H). Found: C, 68.10; H, 9.83; N, 4.80%. Calcd for $C_{16}H_{27}NOS$: C, 68.28; H, 9.67; N, 4.98%.

***N*-Isopropylsulfinyl-3,5-di-*t*-butylaniline (7g):** Yield 1.84 g (6.22 mmol, 64,%); pale yellow prisms; mp 131—132 °C; IR (KBr) 3180 (NH) , 2950—2850 (t-Bu), 1040 cm^{-1} (SO); ^1H NMR ($CDCl_3$) δ=1.28 (s, *t*-Bu, 18 H), 1.31 and 1.35 (each d, J=7 Hz, $CH\underline{Me_2}$, 6 H), 3.04 (sept, J=7 Hz, $C\underline{H}Me_2$, 1 H), 6.8 (br s, NH, 1 H), 6.84—7.07 (m, aromatic, 3 H). Found: C, 69.14; H, 10.02; N, 4.70%. Calcd for $C_{17}H_{29}NOS$: C, 69.09; H, 9.89; N, 4.74%.

Reaction of 7d with DBPO. A solution of 0.681 g (1.87 mmol) of **7d** and 0.500 g (2.13 mmol) of DBPO in 50 ml of benzene was stirred at room temperature (21—24 °C) for one day under nitrogen. The reaction mixture was then washed with a 10% $Na_2S_2O_3$ solution (2×30 ml) and brine (30 ml), and dried over $MgSO_4$. After filtration, the filtrate was concentrated to ca. 10 ml under reduced pressure and chromatographed on silica gel (Wako gel C-200, column size 3.5×35 cm) with benzene as the eluant. 1,1′-Azobis(3,5-di-*t*-butylbenzene) (**10**) and 1,3,5,7-tetra-*t*-butylphenazine (**11**) were first eluted as a mixture, and subsequent elution gave 142 mg (0.250 mmol, 27%) of **8d** and 176 mg (0.463 mmol, 25%) of **9d**. The mixture of **10** and **11** was rechromatographed on silica gel. Elution with hexane gave 2.6 mg (0.0064 mmol, 0.7%) of **11** and subsquent elution with 1:3 benzene-hexane gave 34 mg (0.084 mmol, 9.0%) of **10**. Products **10** and **11** were identified by their IR spectra and melting points; **10**: mp 208—209 °C (lit,[21] 210—212 °C); **11**: mp >305 °C (lit,[21] >305 °C).

***N*-(4-Chlorophenylsulfinyl)-*N*,*N*-bis(3,5-di-*t*-butylphenyl)-hydrazine (8d):** Colorless needles (from hexane); mp 198—199 °C (decomp); IR (KBr) 3030 (NH), 2950—2850 (*t*-Bu), 1085 cm^{-1} (SO); MS (30 eV) m/z (relative intensity) 566 (M^+, 86), 407 (30), 362 (66), 57 (100); ^1H NMR ($CDCl_3$) δ=1.20 (s, *t*-Bu, 36 H), 6.88—7.93 (m, aromatic, 10 H). Found: C, 72.07; H, 8.32; N, 5.00; Cl, 6.39; S, 5.64%. Calcd for $C_{34}H_{47}ClN_2OS$: C, 71.98; H, 8.35; N, 4.94; Cl, 6.25; S, 5.64%.

***N*-(4-Chlorophenylsulfonyl)-3,5-di-*t*-butylaniline (9d):** Colorless needles (from hexane); mp 178—180 °C; IR (KBr) 3230 (NH), 2950—2850 (*t*-Bu), 1170 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ=1.23 (s, *t*-Bu, 18 H), 6.60 (s, NH, 1 H), 6.83—7.67 (m, aromatic, 7 H). Found: C, 63.28; H, 6.86; N, 3.57%. Calcd for $C_{20}H_{26}ClNO_2S$: C, 63.22; H, 6.90; N, 3.69%.

Reaction of 7e with DBPO. In the same manner, **7e** (0.500 g, 1.87 mmol) was treated with 0.500 g (2.13 mmol) of DBPO in benzene (50 ml) at room temperature for one day under nitrogen. After washing ($Na_2S_2O_3$ solution and brine) and drying ($MgSO_4$), the reaction mixture was chromatographed on silica gel with 1:20 ethyl acetate-benzene. Compounds **10** and **11** were first eluted as a mixture, and **8e** (135 mg, 0.287 mmol, 31%) and **9e** (87 mg, 0.307 mmol, 16%) were subsequently eluted. A mixture of **10** and **11** was similarly rechromatographed on silica gel, giving 4.0 mg (0.01 mmol, 1%) of **11** and 46 mg (0.11 mmol, 12%) of **10**. Compound **9e** was identified by its IR and ^1H NMR spectra and melting point [133—135 °C (lit,[7] 134—135 °C)].

***N*-Methylsulfinyl-*N*,*N*′-bis(3, 5-di-*t*-butylphenyl)hydrazine (8e):** Colorless needles (from hexane); mp 144—145.5 °C (decomp); IR (KBr) 3080 (NH), 2950—2850 (*t*-Bu), 1090 cm^{-1} (SO); MS (30 eV) m/z (relative intensity) 470 (M^+, 100), 407 (34), 351 (26), 266 (84), 205 (90), 57 (42); ^1H NMR ($CDCl_3$) δ=1.27 (s, *t*-Bu, 36 H), 3.19 (s, Me, 3 H), 7.03—7.09 (m, aromatic, 6 H). Found: C, 74.01; H, 9.95; N, 5.92%. Calcd for $C_{29}H_{46}N_2OS$: C, 73.99; H, 9.85; N, 5.95%.

Reaction of 8d with DBPO. A solution of 250 mg (0.440 mmol) of **8d** and 125 mg (0.534 mmol) of DBPO in 50 ml of benzene was stirred at room temperature for one day under nitrogen. After washing ($Na_2S_2O_3$ solution and brine) and drying ($MgSO_4$), the reaction mixture was chromatographed on silica gel (column size, 35×35 cm). Elution with 1:1 benzene-hexane gave 98 mg (0.105 mmol, 65% based on the **8d** consumed) of **12**, and elution with benzene gave 66 mg (26%) of **8d**.

1,3-Bis(*p*-chlorophenylsulfinyl)-1,2,3-tris(3,5-di-*t*-butylphenyl)triazane (12): Colorless prisms (from hexane); mp 146—149 °C (decomp); IR (KBr) 2950—2850 (*t*-Bu), 1070 cm^{-1} (SO); ^1H NMR ($CDCl_3$) δ=0.89 (s, *t*-Bu, 18 H), 1.09 (s, *t*-Bu, 36 H), 6.40 (d, J=1 Hz, *o*-H of N^2-phenyl group, 2 H), 6.57 (d, J=1 Hz, *o*-H of N^1- and N^3-phenyl groups, 4 H), 6.89 (br t, *p*-H of N^1- and N^3-phenyl groups, 2H), 7.03 (br t, *p*-H of N^2-phenyl group, 1 H), 7.54 (d, J=9 Hz, C_6H_4SO, 4 H), 8.33 (d, J=9 Hz, C_6H_4SO, 4 H). Found: C, 70.88; H, 8.41; N, 4.16%. Calcd for $C_{60}H_{85}Cl_2N_3O_2S_2$ (**12**+hexane):[22] C, 70.98; H, 8.43; N, 4.16%.

ESR Measurements. The ESR samples were prepared as

follows: 20—30 mg of **7**, 40—50 mg of DBPO, and 0.40 ml of benzene were placed in an ESR cell; the mixture was degassed by three freeze-pump-thaw cycles using a high-vacuum system, and the cell was sealed off from the vacuum system. The ESR spectra were recorded at 21 or 40 °C with a JEOL JES-ME-3X spectrometer equipped with an X-band microwave unit and 100-kHz field modulation. The hyperfine splitting constants and g values were determined by simulutaneous measurements with a dilute Fremy's salt in K_2CO_3 aqueous solution (a_N=1.309 mT, g=2.0055).

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