Calcd for $C_{12}H_{19}Cl_2NOPt$: C, 31.38; H, 4.17; N, 3.05. Found: C, 31.02; H, 4.30; N, 3.16.

By the same procedure, complex **1a** was also prepared from an excess of the ethylene complex with respect to the α-methylallyl alcohol (molar ratio 1.5:1) in $CHCl_3$ solution. In this case, the isolated solid was a mixture of **1a** and unreacted ethylene complex.

Complexes 1b-f. Complexes **1b-f** were obtained via the procedure described for complex **1a**. In all cases ethylene was substituted quantitatively by the unsaturated ether or alcohol. The complexes were crystallized from $CHCl_3$/pentane (1:2), yields after crystallization being about 60-70%. Elemental analyses and melting points of the crystallized complexes are as follows.

1b: mp 129 °C. Anal. Calcd for $C_{14}H_{23}Cl_2NOPt$: C, 34.50; H, 4.75; N, 2.87. Found: C, 34.22; H, 4.51; N, 3.07.

1c: mp 123 °C. Anal. Calcd for $C_{15}H_{25}Cl_2NOPt$: C, 35.93; H, 5.03; N, 2.79. Found: C, 35.22; H, 5.42; N, 2.53.

1d: mp 151 °C. Anal. Calcd for $C_{17}H_{21}Cl_2NOPt$: C, 39.17; H, 4.06; N, 2.69. Found: C, 40.24; H, 4.23; N, 2.51.

1e: mp 110 °C. Anal. Calcd for $C_{13}H_{21}Cl_2NOPt$: C, 32.99; H, 4.47; N, 2.96. Found: C, 32.87; H, 4.54; N, 2.42.

1f: mp 92 °C. Anal. Calcd for $C_{15}H_{25}Cl_2NOPt$: C, 35.93; H, 5.03; N, 2.79. Found: C, 34.57; H, 5.12; N, 2.31.

NMR Measurements. NMR spectra were recorded in acetone-d_6 on a Varian VXR-300 spectrometer operating at 64.3 MHz for ^{195}Pt. The ^{195}Pt resonance of *cis*-dichloro[(*S*)-α-methylbenzylamine](ethylene)platinum(II) is at higher field (-2780 ppm) than the absorptions due to complexes **1a-f**. All ^{195}Pt NMR chemical shifts are referenced to Na_2PtCl_6 as external standard.

Thioaminyl Diradicals: An Electron Spin Resonance Spectroscopic Study[1]

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In a series of electron spin resonance (ESR) spectroscopic studies of a new class of nitrogen-centered free radicals, we have found that thioaminyls (RNSR′) are persistent nitrogen-centered free radicals. For instance, some thioaminyls have been isolated as radical crystals[2] or hydrazine-like dimers, which dissociate in solution into the corresponding radicals at room temperature.[3,4] These interesting persistent properties of thioaminyls can be interpreted as a result of significant stabilization of radicals by conjugative delocalization of the unpaired electron from nitrogen to sulfur.

The present work is concerned with an ESR study of aromatic thioaminyl diradicals,[5] which has been performed as part of a program directed toward the syntheses of organic ferromagnetic materials. In the present study we have found that thioaminyl diradicals in solution exists as diradical oligomers, which are in equilibrium with diamagnetic cyclic compounds that can be isolated as crystals. Herein we report generation of thioaminyl diradicals and their ESR spectra and isolation of the cyclic compounds and their characterization.

(1) ESR studies of nitrogen-centered free radicals 33. Part 32: Miura, Y.; Ohonishi, T. *J. Org. Chem.* **1988**, *53*, 3012-3016.
(2) Miura, Y.; Yamamoto, A.; Katsura, Y.; Kinoshita, M.; Sato, S.; Tamura, C. *J. Org. Chem.* **1982**, *47*, 2618-2622.
(3) Miura, Y.; Yamamoto, A.; Katsura, Y.; Kinoshita, M. *J. Org. Chem.* **1980**, *45*, 3875-3880.
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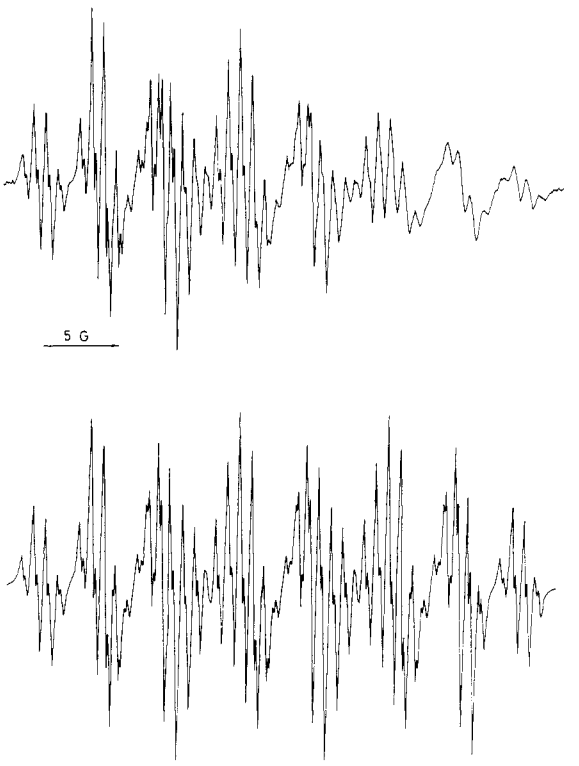
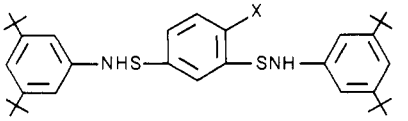


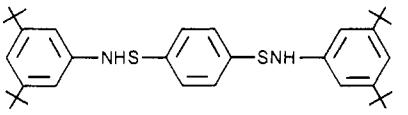
Figure 1. Experimental ESR spectrum of **3a** detected from a solution of **5a** in benzene at 17 °C (top) and computer-simulated ESR spectrum reconstructed by using the parameters listed in Table I (bottom).

Results and Discussion

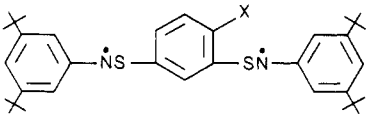
Thioaminyl diradicals **2** were generated by oxidation of precursors **1** with PbO_2. When PbO_2 was added to a stirred solution of **1** in benzene, the colorless solution immediately turned dark blue or dark greenish blue and the resulting colored solution gave an intense ESR signal. An ESR



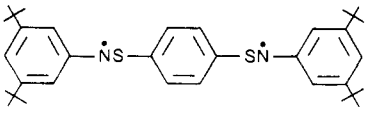
1a: X = H
b: X = Cl



1c



2a: X = H
b: X = Cl



2c

spectrum from a dilute solution of **2a** is illustrated in Figure 1. Although the radical solution was, after removal of the PbO_2, allowed to stand at room temperature for 1 day, the blue color still remained without fading. This observation indicates that the thioaminyl diradicals are

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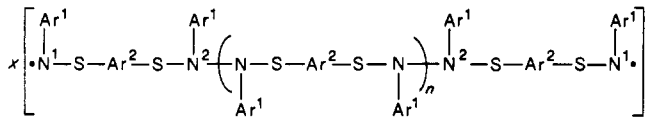
Table I. ESR Parameters and λ_{max} for Diradical Oligomers 3[a-c]

radical	a_N	$a_{o\text{-}H}$[d,e]	$a_{p\text{-}H}$[d,e]	$a_{o\text{-}H}$[e,f]	$a_{m\text{-}H}$[e,f]	$a_{p\text{-}H}$[e,f]	a_{other}	g	λ_{max}, nm
3a	9.61	3.74 (2)	4.28 (1)	0.77 (2)	0.28 (1)	0.77 (1)	10.3 (^{13}C)[g,h]	2.0058	598
3b	9.59	3.94 (2)	4.69 (1)	0.78 (1 or 2)		0.78 (1 or 0)	10.4 (^{13}C)[g,h]	2.0056	598
3c	9.49	3.63 (2)	4.15 (1)	0.79 (2)	0.26 (2)		0.11 (N^2), 10.0 (^{13}C),[g,h] 4.6 (^{33}S)[i]	2.0059	630
4[j]	9.53	3.71	4.22	0.76	0.27	0.83	10.34 (^{13}C),[k] 5.44 (^{13}C),[k] 4.62 (^{33}S)[k]	2.0060	597

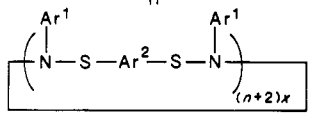
[a] Hyperfine splitting constants have been determined by computer simulation and are given in gauss. [b] Solvent, benzene. [c] Temperature, 17 ± 1 °C. [d] Protons on the anilino benzene ring. [e] Numbers in parentheses refer to the number of equivalent protons. [f] Protons on the phenylthio benzene ring. [g] ^{13}C at natural abundance. [h] Assigned to one carbon based on the intensity ratio to the parent spectrum. [i] ^{33}S at natural abundance. [j] Taken from ref 3. [k] The values for the deuteriated radical, see ref 3.

substantially persistant in solution and are not destroyed by oxygen.

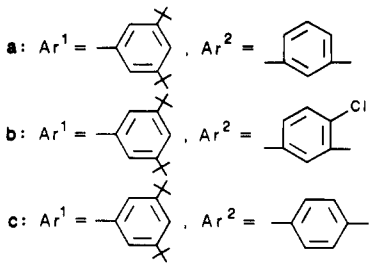
Although the right-hand (high field) halves of the experimental ESR spectra are significantly broadened, probably owing to the lack of sufficient molecular motions of radicals (see Figure 1), the left-hand (low field) halves are well resolved and could be satisfactorily reconstructed by computer simulation with use of hyperfine splitting (hfs) constants listed in Table I, provided that there is no or negligibly weak spin-exchange interaction between the two spins. This means that the ESR spectra obtained are not attributable to **2** but originate from dimers or longer oligomers of **2** (**3**) in which the two spins are separated far



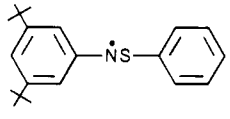
3



5



enough to render spin-exchange interaction negligible. Accordingly, the hfs constants for **3** are essentially the same as those for thioaminyl monoradical **4**.[3] However, upon more detailed examination of the hfs constants, one may note that the $a_{o\text{-}H}$ and $a_{p\text{-}H}$ values for the anilino benzene ring protons of **3b** are somewhat higher than those for the corresponding protons of **3a**, **3c**, and **4**. The increases of



4

$a_{o\text{-}H}$ and $a_{p\text{-}H}$ can, however, be easily accounted for in terms of an increase in the relative importance of canonical structure A, which seems to result from the presence of an electron-withdrawing chlorine atom in the SC_6H_4S group. Interestingly, in the spectrum of **3c** the hfs due to N^2 of 0.11 G was observed, indicating that in **3c** the

A B

unpaired electron is delocalized until N^2 across the SC_6H_4S group. In **3a** and **3b** such extensive delocalization of the unpaired electron was not observed. This is probably due to the 1,3-disubstituted structure of the SC_6H_4S group.

When a solution of **3** was heated to a high temperature, the ESR signal became strong, and when cooled to room temperature, it became weak, and this cycle was completely reversible. This indicates that diradical oligomers **3** in solution exist in equilibrium with diamagnetic compounds. We have tried to isolate the compounds and have found that they can be isolated as light blue microprisms (**5a** and **5b**) or light blue needles (**5c**), having a sharp melting point, in 16–40% yield from benzene solutions of **3** after removal of the solvent by freeze-drying and subsequent careful crystallization of the residue. Although the IR spectra of the isolated crystals as a whole are very similar to the corresponding spectrum of precursors **1**, no N–H absorption was found in the region 3380–3350 cm^{-1}. Also, the elemental analyses of the crystals indicated the structure of $(2)_n$. On the basis of these results it was concluded that the compounds isolated have the cyclic structure represented as **5**.

When the cyclic compounds **5** were dissolved in benzene at room temperature, the resulting solution immediately turned dark blue (λ_{max}, see Table I) and gave an intense ESR signal due to **3**. This observation clearly indicates that compounds **5**, upon dissolution, dissociate into **3** at room temperature. Although a sufficiently dilute solution of **5** was heated to 80 °C, no detectable change in the ESR spectra was found except broadening of the spectra and signals that appeared to be attributable to monomeric diradicals **2** were not detected.

Since the values of n and x in compounds **3** and **5** are unknown, equilibrium constants for the equilibria $\mathbf{5} \rightleftarrows 2(\mathbf{3})$ cannot be determined. However, it will be possible to compare roughly the degrees of dissociation of **5** into **3** from the numbers of the spins generated by dissociation of **5**. When compounds **5** (0.475 mmol of monomer units) were dissolved in benzene (total volume, 25 mL) at room temperature, the numbers of spins in the resulting solutions were 7.8×10^{17} (**5a** and **5b**) and 4.6×10^{19} (**5c**), respectively, the results suggesting that the degrees of dissociation of **5a** and **5b** were almost the same and that of **5c** was much larger than those for **5a** and **5b**.

In conclusion, substantially persistent and oxygen-insensitive thioaminyl diradicals **2** were generated by oxidation of **1** with PbO_2. The diradicals in solution exist as diradical oligomers **3**, which can be isolated as diamagnetic cyclic compounds. The compounds, upon dissolution, dissociate into **3** at room temperature.

Experimental Section

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Infrared (IR) spectra were run on a JASCO A-202 spectrophotometer, and visible spectra were run on a Simadzu UV-240 spectrophotometer. Proton neuclear magnetic reonance (^{1}H NMR) spectra were recorded with a JEOL PS-100 spectrometer (100 MHz). Chemical shifts (δ) are

expressed in parts per million downfield from tetramethylsilane as internal standard. Column chromatography was performed on alumina (Merck aluminium oxide 90) with benzene as eluant. 3,5-Di-*tert*-butylaniline was prepared by the reported method.[6]

***N,N'*-Bis(3,5-di-*tert*-butylphenyl)-1,3-benzenedisulfenamide (1a).** 1,3-Benzenedithiol (1.00 g, 7.03 mmol) was dissolved in 14 mL of dry CH_2Cl_2. To the solution was added dropwise at room temperature a solution of 2.35 g (17.4 mmol) of SO_2Cl_2 in 5 mL of dry CH_2Cl_2 with stirring. The resulting mixture was heated at reflux for 1.5 h with stirring, giving a homogeneous orange solution. The solvent and the excess SO_2Cl_2 were removed in vacuo, and the resulting orange oil (benzene-1,3-disulfenyl chloride) was dissolved in 30 mL of dry ether. The ethereal solution was then added dropwise to a stirred solution of 3.18 g (15.5 mmol) of 3,5-di-*tert*-butylaniline and 2.1 g (21 mmol) of Et_3N in 150 mL of dry ether at 0 °C. After being stirred for 1 h at 0 °C, the reaction mixture was filtered, evaporated, and passed through a short alumina column to remove polar byproducts. Crystallization from hexane yielded 1.89 g (3.44 mmol, 49%) of colorless needles with mp 137–139 °C: IR (KBr) 3380 (NH), 2950–2850 cm^{-1} (*t*-Bu); ^1H NMR ($CDCl_3$) δ 1.27 (s, *t*-Bu, 36 H), 5.07 (s, NH, 2 H), 6.85–7.35 (m, aromatic, 10 H). Anal. Calcd for $C_{34}H_{48}N_2S_2$: C, 74.40; H, 8.81; N, 5.11. Found: C, 74.15; H, 8.82; N, 4.76.

***N,N'*-Bis(3,5-di-*tert*-butylphenyl)-4-chloro-1,3-benzenedisulfenamide (1b).** 1,3-Benzenedithiol (1.00 g, 7.03 mmol) was dissolved in 50 mL of dry CH_2Cl_2, and chlorine gas was bubbled in a steady stream through the solution at −10 °C until the solution became orange and homogeneous (ca. 30 min). Excess chlorine gas and the solvent were removed in vacuo, giving an orange oil of 4-chlorobenzene-1,3-disulfenyl chloride.[7] The disulfenyl chloride was dissolved in 30 mL of dry ether, and the solution was added dropwise to a stirred solution of 3.18 g (15.5 mmol) of 3,5-di-*tert*-butylaniline and 2.1 g (21 mmol) of Et_3N in 150 mL of dry ether at 0 °C. After being stirred for 1 h at 0 °C, the reaction mixture was filtered, evaporated, and passed through a short alumina column to remove polar byproducts. Crystallization from hexane yielded 1.41 g (2.42 mmol, 34%) of colorless needles with mp 92–96°C: IR (KBr) 3350 (NH), 2950–2850 cm^{-1} (*t*-Bu); ^1H NMR ($CDCl_3$) δ 1.26 and 1.29 (each s, *t*-Bu, 36 H), 4.51 and 4.93 (each s, NH, 2 H), 6.76–7.20 (m, aromatic, 9 H). Anal. Calcd for $C_{34}H_{47}ClN_2S_2$: C, 70.00; H, 8.12; N, 4.80; Cl, 6.08. Found: C, 69.58; H, 8.14; N, 4.68; Cl, 5.93.

***N,N'*-Bis(3,5-di-*tert*-butylphenyl)-1,4-benzenedisulfenamide (1c).** In a manner analogous to the above, 1.00 g (7.03 mmol) of 1,4-benzenedithiol was treated with 2.35 g (17.4 mmol) of SO_2Cl_2, and benzene-1,4-disulfenyl chloride, obtained as orange crystals after removal of the solvent, was allowed to react with 3.18 g (15.5 mmol) of 3,5-di-*tert*-butylaniline in ether in the presence of Et_3N. After column chromatography, the product was crystallized from hexane to give 1.91 g (3.48 mmol, 50%) of light pink prisms with mp 193–195 °C dec: IR (KBr) 3380 (NH), 2950–2850 cm^{-1} (*t*-Bu); ^1H NMR ($CDCl_3$) δ 1.26 (s, *t*-Bu, 36 H), 5.07 (s, NH, 2 H), 6.84–7.18 (m, aromatic, 10 H). Anal. Calcd for $C_{34}H_{48}N_2S_2$: C, 74.40; H, 8.81; N, 5.11. Found: C, 74.16; H, 8.87; N, 5.12.

This compound was also prepared in 58% yield by reaction of 3,5-di-*tert*-butylaniline with benzene-1,4-disulfenyl chloride obtained by bubbling chlorine gas into a solution of 1,4-benzenedithiol in dry CH_2Cl_2 at −10 °C.

General Procedure for Isolation of Cyclic Compounds 5. Compound 1 (500 mg) was dissolved in 20 mL of benzene with stirring. To the solution was added 3.0 g of anhydrous K_2CO_3, and stirring was continued. PbO_2 (4.0–5.0 g) was then added in four portions to the stirred mixture over a period of 3–4 min, and stirring was continued for an additional 1 min. After filtration, the solvent was removed by freeze-drying, and ca. 2 mL mL of hexane was added to the blue microcrystalline residue. Upon cooling of the mixture to −20 °C overnight, light blue microcrystals were given, which were collected by filtration, and again recrystallized from hexane (**5c**) or 1:10 benzene–hexane (**5a** and **5b**).

5a: light blue microprisms; mp 143–145 °C dec; yield 198 mg (40%); IR (KBr) 2950–2850, 1580, 1475, 1455, 1420, 1385, 1360, 1300, 1240, 1200, 980, 855, 765, 705, 680 cm^{-1}. Anal. Calcd for $(C_{34}H_{46}N_2S_2)_n$: C, 74.68; H, 8.48; N, 5.12. Found: C, 74.42; H, 8.70; N, 5.05.

5b: light blue microprisms; mp 155–158 °C dec; yield 79 mg (16%);[9] IR (KBr) 2950–2850, 1580, 1475, 1445, 1420, 1360, 1300, 1245, 1200, 1025, 980, 855, 800, 705 cm^{-1}. Anal. Calcd for $(C_{34}H_{45}ClN_2S_2)_n$: C, 70.25; H, 7.80; N, 4.82. Found: C, 70.47; H, 7.84; N, 4.77.

5c: light blue needles; mp 132–134 °C dec; yield 86 mg (17%); IR (KBr) 2950–2850, 1580, 1470, 1420, 1390, 1360, 1295, 1245, 1200, 980, 860, 810, 708 cm^{-1}. Anal. Calcd for $(C_{34}H_{46}N_2S_2)_n$: C, 74.68; H, 8.48; N, 5.12. Found: C, 74.43; H, 8.30; N, 4.91.

Measurements of ESR Spectra. ESR samples were prepared by the following two methods. (1) A mixture of 20 mg of **1**, 200 mg of anhydrous K_2CO_3, and 200 mg of PbO_2 in 5 mL of benzene was stirred for 2–4 min. After filtration, 0.20 mL of the filtrate was placed in an ESR cell, the solution was degassed by three freeze–pump–thaw cycles with a high vacuum system, and the cell was sealed off. (2) In the same manner as above, 0.5–5.0 mg of **5** and 0.40 mL of benzene were placed in an ESR cell, the solution was degassed, and the cell was sealed off.

ESR spectra were recorded with a JEOL JES-ME-3X spectrometer equipped with an X-band microwave unit and 100 kHz field modulation. Hyperfine splitting constants and *g* values were determined by comparison with Fremy's salt in aqueous K_2CO_3 solution (a_N, 13.09 G; *g*, 2.0057). Estimated accuracy: ±0.1 G for a_N and a_H, ±0.2 G for $a_{^{13}C}$ and $a_{^{33}S}$, and ±0.0002 for *g*. The temperatures of the ESR cavity were controlled with JEOL JES-VT-3 apparatus and determined with a copper-constantan thermocouple. Spin concentrations were determined by weighing the areas of integrated ESR spectra obtained with a JEOL JES-ID-2 integrator.[3] Calibration curves were drawn with 1,3,5-triphenylverdazyl solutions in benzene.

Acknowledgment. We thank Seitetsu Kagaku Co., Ltd., for the gift of 1,4-benzenedithiol.

(6) Allinger, N. L.; Blatter, H. M.; Freiberg, L. A.; Karkowski, F. M. *J. Am. Chem. Soc.* **1966**, *88*, 2999–3011.

(7) In a previous paper[8] it was reported that chlorination of 1,3-benzenedithiol with Cl_2 gave benzene-1,3-disulfenyl chloride. In our case, however, the same reaction gave 4-chlorobenzene-1,3-disulfenyl chloride.

(8) Feher, F.; Malcharek, F.; Glinka, K. *Z. Naturforsch.* **1971**, *26B*, 67–68.

(9) Sufficiently pure crystals of **5b** were given in 70% yield by washing the residue with hexane after the benzene was removed by freeze-drying.

Synthesis of the Hexacyclic Indole Alkaloid (±)-Kopsijasmine

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(−)-Kopsijasmine, **1**, the 16,17-dehydro analogue of pleiocarpine **2**, was recently isolated from *Kopsia Jaminiflora Pitard*, and its structure was determined largely from NMR data.[1] Here we report the total synthesis of (±)-**1** via the 3-chloro heptacyclic kopsane derivative **11**.

The known homoannular diene **3**[2] was treated with KH/THF/0 °C, followed by 1-iodo-2-chloroprop-2-ene to give **4** in 92% yield (Scheme I). It should be noted that the alkylation of the C-11 carbanion derived from **3** always takes place on the endo face, as originally reported in the synthesis of kopsanone.[2] In general, nonplanar amides appear to undergo alkylation on the face opposite the pyramidalized nitrogen lone pair of electrons. Recently,

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