Stable Thioaminyl Radicals Having Functional Groups: Generation, ESR Spectra, Isolation, X-ray Crystallographic Analyses, and Magnetic Characterization of *N*-(Arylthio)-4-(ethoxycarbonyl)-2,6-diarylphenylaminyls, *N*-(Arylthio)-4-acetyl-2,6-diarylphenylaminyls, and *N*-(Arylthio)-4-cyano-2,6-diarylphenylaminyls[1]

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Oxidation of *N*-(arylthio)-4-(ethoxycarbonyl)-2,6-diarylanilines (**9**), *N*-(arylthio)-4-acetyl-2,6-diarylanilines (**10**), and *N*-(arylthio)-4-cyano-2,6-diarylanilines (**11**) with PbO_2 yielded quite persistent *N*-(arylthio)-4-(ethoxycarbonyl)-2,6-diarylphenylaminyls (**4**), *N*-(arylthio)-4-acetyl-2,6-diarylphenylaminyls (**5**), and *N*-(arylthio)-4-cyano-2,6-diarylphenylaminyls (**6**), respectively, and they were isolated as pure radical crystals. On the other hand, *N*-(arylthio)-4-nitro-2,6-diarylphenylaminyls (**6**), and *N*-(arylthio)-4-chloro-2,6-diarylphenylaminyls (**7**), were unstable and soon decomposed. The X-ray crystallographic analyses of *N*-[(2,4-dichlorophenyl)thio]-4-acetyl-2,6-diphenylphenylaminyl (**5c**) and *N*-[(2,4-dichlorophenyl)thio]-4-cyano-2,6-diphenylphenylaminyl (**6c**) showed that the Ph−N−S−Ph π-framework is planar, and the 2- and 6-phenyl groups are twisted from the coplane. The ESR studies for **4**−**8** showed that their hyperfine coupling constants are nearly identical to each other and that the unpaired electron is extensively delocalized onto the anilino benzene ring and the arylthiyl group. The magnetic susceptibility measurements were carried out for five thioaminyl radical crystals and showed that one radical couples ferromagnetically with $2J/k_B = 16.0$ K, and the other four radicals couple antiferromagnetically with $2J/k_B = -15.6$ to -194.6 K or $\theta = -0.6$ to -5.0 K.

Introduction

Although free radicals are generally transient due to an electron vacancy in the highest occupied molecular orbital, electronic stabilization and steric protection can render them isolable. The well-known examples are nitroxides, verdazyls, diphenylpicrylhydrazyl, and 2,4,6-tri-*tert*-butylphenoxyl,[2] which are well-known as the isolable stable free radicals. In recent years, isolable stable free radicals have attracted much attention in the studies of molecule-based magnetism[3] and "living" free radical polymerization.[4]

In previous papers we reported that *N*-(arylthio)-2,4,6-triarylphenylaminyls (**1**), *N*-(arylthio)-4-*tert*-butyl-2,6-diarylphenylaminyls (**2**), and *N*-(arylthio)-2-*tert*-butyl-4,6-diarylphenylaminyls (**3**) are quite persistent radicals, and that, when having appropriate electron-withdrawing substituents such as nitro or chloro in the phenylthiyl group, they can be isolated as radical crystals (Chart 1).[5−8] The magnetic measurements for the isolated thioaminyl radicals carried out using solid radical crystals showed that, although most thioaminyl radicals couple antiferromagnetically, three radicals couple ferromagnetically with the magnetic exchange interactions of $2J/k_B = 3.6-28.0$ K.[9]

In the present study we prepared *N*-(arylthio)-4-(ethoxycarbonyl)-2,6-diarylphenylaminyls (**4**), *N*-(arylthio)-4-acetyl-2,6-diarylphenylaminyls (**5**), *N*-(arylthio)-4-cyano-2,6-diarylphenylaminyls (**6**), *N*-[(2,4-dichlorophenyl)thio]-

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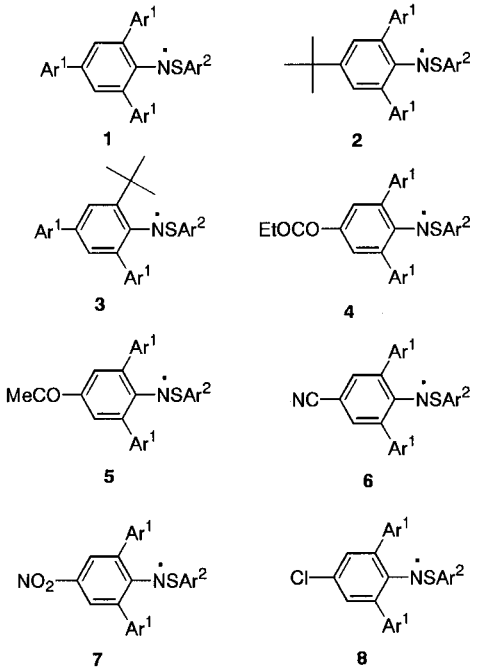
Chart 1

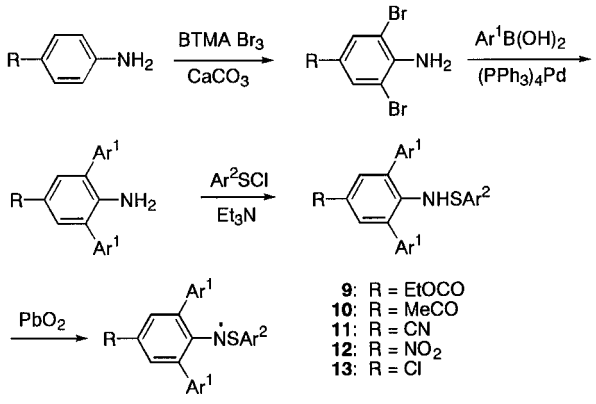


4-nitro-2,6-diphenylphenylaminyls (**7**), and *N*-[(2,4-dichlorophenyl)thio]-4-chloro-2,6-diphenylphenylaminyls (**8**) (Chart 1). The structures show that the present thioaminyls have an electron-withdrawing substituent such as ethoxycarbonyl, acetyl, cyano, nitro, or chloro at the anilino para position. If these radicals are sufficiently stable to be isolated, a variety of isolable stable thioaminyl radicals including di- and triradicals can be prepared by using the functional groups. Herein we report generation, stabilities, ESR spectra, isolation, X-ray crystallographic analyses, and magnetic behavior of **4**−**6**.

Results and Discussion

Preparation of Precursors 9−13. The corresponding precursors of **4**−**7**, *N*-(arylthio)-4-(ethoxycarbonyl)-2,6-diarylanilines (**9**), *N*-(arylthio)-4-acetyl-2,6-diarylanilines (**10**), *N*-(arylthio)-4-cyano-2,6-diarylanilines (**11**), *N*-[(2,4-dichlorophenyl)thio]-4-nitro-2,6-diphenylaniline (**12**), and *N*-[(2,4-dichlorophenyl)thio]-4-chloro-2,6-diphenylaniline (**13**) were prepared according to Scheme 1. Thus, treatment of 4-(ethoxycarbonyl)aniline, 4-acetylaniline, 4-cyanoaniline, or 4-chloroaniline with benzyltrimethylammomium tribromide (BTMA·Br_3) in CH_2Cl_2−MeOH in the presence of $CaCO_3$ gave 4-(ethoxycarbonyl)-2,6-dibromoaniline in 80%, 4-acetyl-2,6-dibromoanilione in 83%, 4-cyano-2,6-dibromoaniline in 81%, and 4-chloro-2,6-dibromoaniline in 93% yields,[10] respectively. 4-Nitro-2,6-dibromoaniline was commercially available. The palladium-catalyzed cross-coupling reaction of the dibromoanilines with arylboronic acid yielded 4-(ethoxycarbonyl)-2,6-diarylanilines in 87−90%, 4-acetyl-2,6-diarylanilines in 60−72%, 4-cyano-2,6-diphenylaniline in 80, 4-nitro-2,6-diphenylaniline in 95%, and 4-chloro-2,6-diphenylaniline in 73% yield,[11] respectively. The reaction

Scheme 1



4a, **9a**: Ar^1 = Ph, Ar^2 = 3-$NO_2C_6H_4$
4b, **9b**: Ar^1 = Ph, Ar^2 = 4-$NO_2C_6H_4$
4c, **9c**: Ar^1 = Ph, Ar^2 = 2,4-$Cl_2C_6H_3$
4d, **9d**: Ar^1 = Ph, Ar^2 = 3,5-$Cl_2C_6H_3$
4e, **9e**: Ar^1 = 4-ClC_6H_4, Ar^2 = 3-$NO_2C_6H_4$
4 f, **9 f**: Ar^1 = 4-ClC_6H_4, Ar^2 = 4-$NO_2C_6H_4$
4g, **9g**: Ar^1 = 4-ClC_6H_4, Ar^2 = 2,4-$Cl_2C_6H_3$
4h, **9h**: Ar^1 = 4-ClC_6H_4, Ar^2 = 3,5-$Cl_2C_6H_3$
5b, **10b**: Ar^1 = Ph, Ar^2 = 4-$NO_2C_6H_4$
5c, **10c**: Ar^1 = Ph, Ar^2 = 2,4-$Cl_2C_6H_3$
5g, **10g**: Ar^1 = 4-ClC_6H_4, Ar^2 = 2,4-$Cl_2C_6H_3$
6c, **11c**: Ar^1 = Ph, Ar^2 = 2,4-$Cl_2C_6H_3$
6d, **11d**: Ar^1 = Ph, Ar^2 = 3,5-$Cl_2C_6H_3$
7, **12**: Ar^1 = Ph, Ar^2 = 2,4-$Cl_2C_6H_3$
8, **13**: Ar^1 = Ph, Ar^2 = 2,4-$Cl_2C_6H_3$

of the 4-substituted 2,6-diarylanilines with arenesulfenyl chlorides in dry ether or anhydrous THF in the presence of Et_3N gave **9** in 26−54%, **10** in 48−58%, **11** in 54−90%, **12** in 8%, and **13** in 55% yields, after column chromatographic separation and subsequent crystallization.[12]

Although precursors **9e**−**h**, **10**, **11**, **12**, and **13** could be readily purified by recrystallization from the appropriate solvents, crystallization of **9a**−**d** were unsuccessful, giving a noncrystalline powder or viscous solid containing small amounts of impurities. This is probably due to the presence of a flexible ethyl ester group. We were therefore forced to use the crude precursors in the next oxidation step without any further purification as described below. The analytical samples of **9a**−**d** were obtained by the preparative GPC purification and subsequent crystallization.

Generation of 4−8 and Their ESR Spectra. Oxidation of **9**−**13** was carried out in benzene with PbO_2. When the ethoxycarbonyl, acetyl, and cyano substituted precursors **9**−**11** were treated with PbO_2, the solution immediately turned dark blue (**4a**,**c**−**e**,**g**−**h**, **6**) or dark green (**4b**,**f**, **5**) and gave an intense EPR signal due to **4**, **5**, or **6**. The characteristic dark blue or dark green colors were constant at room temperature over a long period without decomposition, even in the presence of atmospheric oxygen, indicating that the generated thioaminyls are quite persistent and oxygen-insensitive radicals. On

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(12) The yields of **9a**−**d** were determined after column chromatographic separation without recrystallizing.

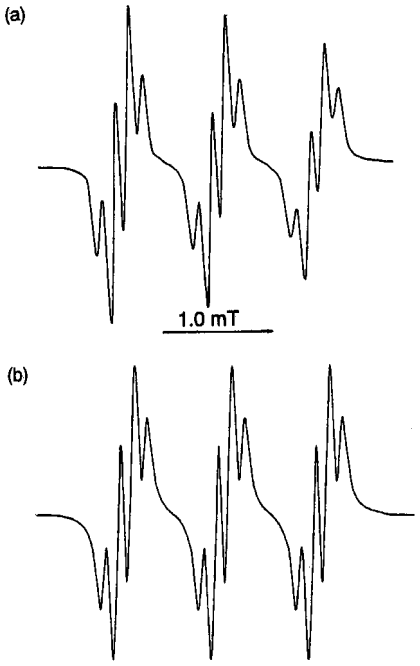


Figure 1. ESR spectra of **5c** in benzene at 20 °C. (a) The experimental ESR spectrum; (b) computer simulation.

the other hand, the nitro- and chloro-substituted precursors, **12** and **13**, yielded unstable radicals on oxidation. When **12** or **13** were treated with PbO_2, the light yellow (**12**) or colorless solution (**13**) immediately turned green (**7**) or blue (**8**), but the characteristic green or blue color soon faded and finally turned dark red. From this color change the corresponding radicals, **7** and **8**, were shown to be unstable.

The ESR spectra of **4**−**8** were recorded at room temperature (20 °C) using benzene as the solvent. Although **4**, **5**, and **6** gave intense and clean ESR spectra, those of **7** and **8** were very weak, and only ESR spectra with a low S/N ratio were obtained. A typical ESR spectrum is shown in Figure 1 and the ESR parameters are summarized in Table 1.

All the ESR spectra were split into a 1:1:1 triplet with nearly identical hyperfine coupling constants in the range 0.873−0.914 mT. In the cases of **4b**, **4f**, **5b**, **7**, and **8** no further hyperfine splittings due to protons were observed. On the other hand, **4c**, **4g**, **5c**, **5g** showed hyperfine splittings due to the anilino meta and phenylthiyl ortho protons, giving spectra consisting of a 1:1:1 triplet of 1:3:3:1 quartets (see: Figure 1), and **4a**, **4d**, **4e**, **4h** showed hyperfine splittings due to the anilino meta and phenylthiyl ortho and para protons, giving spectra consisting of a 1:1:1 triplet of 1:5:10:10:5:1 sextets. In the ESR spectra of **6c** and **6d** the 1:1:1 triplets were split into quintets (not quartets) (**6c**) or septets (not sextets) (**6d**), suggesting an appearance of the hyperfine splitting due to the cyano nitrogen. Although a 1:1:1 hyperfine splitting due to the cyano nitrogen was not clearly observed, the ESR spectra obtained were well reconstructed by computer simulation by adding the hyperfine splitting of 0.065 (**6c**) or 0.066 mT (**6d**) due to the cyano nitrogen.

To confirm the assignments for the proton hyperfine splittings, 2- and 6-phenyl deuterated thioaminyls, **4i** and **5i**, were prepared from 4-(ethoxycarbonyl)- or 4-acetyl-2,6-di(phenyl-d_5)aniline according to the same procedure

Table 1. ESR Spectral Data for 4−8 in Benzene at 20 °C

radical	a_N/mT	a_H/mT[a]	g
4a[b]	0.893	0.128 (2H),[c] 0.093 (3H)[d]	2.0059
4b[e]	0.893		2.0059
4c[b]	0.891	0.132 (2H),[c] 0.097 (1H)[f]	2.0060
4d[b]	0.888	0.125 (2H),[c] 0.091 (3H)[d]	2.0059
4e[b]	0.890	0.128 (2H),[c] 0.091 (3H)[d]	2.0060
4f[e]	0.891		2.0060
4g[b]	0.891	0.133 (2H),[c] 0.096 (1H)[f]	2.0061
4h[b]	0.886	0.125 (2H),[c] 0.093 (3H)[d]	2.0059
4i[b,g]	0.889	0.132 (2H),[c] 0.098 (1H)[f]	2.0060
5b[e]	0.881		2.0060
5c[b]	0.876	0.132 (2H),[c] 0.097 (1H)[f]	2.0061
5g[b]	0.876	0.132 (2H),[c] 0.097 (1H)[f]	2.0062
5i[b,h]	0.877	0.132 (2H),[c] 0.097 (1H)[f]	2.0061
6c[b,i]	0.876	0.130 (2H),[c] 0.099 (1H)[f]	2.0060
6d[b,j]	0.875	0.128 (2H),[c] 0.093 (3H)[d]	2.0057
7[e]	0.873		
8[e]	0.914		

[a] The number in parentheses refers to the number of magnetically equivalent protons. [b] The hyperfine coupling (hfc) constants are determined by computer simulation. [c] The hfc constants due to the anilino meta protons. [d] The hfc constants due to the phenylthiyl ortho and para protons. [e] Hfc constants due to protons are not determined because of the poor resolution. [f] The hfc constants due to the phenylthiyl ortho protons. [g] a^{33}_S = 0.55 mT, and a^{13}_C (1C) = 1.02 mT. [h] a^{33}_S = 0.54 mT, and a^{13}_C (1C) = 1.01 mT. [i] a_N (CN) = 0.065 mT. [j] a_N (CN) = 0.066 mT.

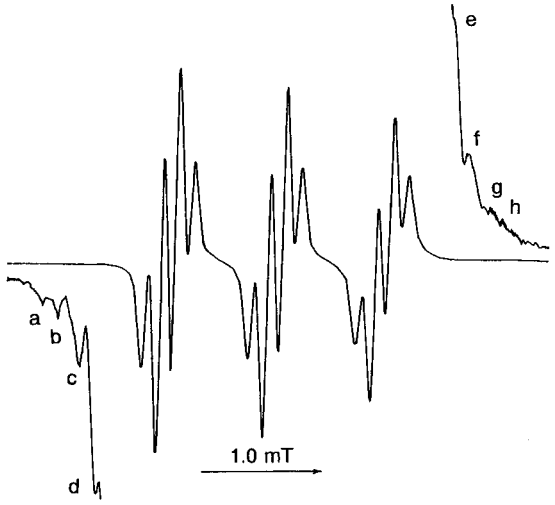
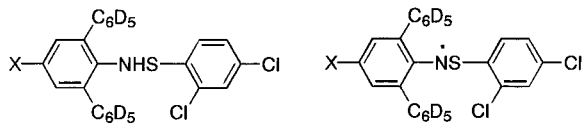


Figure 2. ESR spectrum of **5i** in benzene at 20 °C. Both wings are recorded at high gain (100 times). Satellite lines due to ^{33}S (a and b, $M_N = +1$, $M_S = +3/2$; g and h, $M_N = -1$, $M_S = -3/2$) and ^{13}C (c and d, $M_N = +1$, $M_C = +1/2$; $M_N = -1$, $M_C = -1/2$) were observed.

Chart 2



9i: X = EtOCO
10i: X = MeCO

4i: X = EtOCO
5i: X = MeCO

as for the corresponding nondeuterated compounds (Chart 2). The ESR spectrum of **4i** is shown in Figure 2. As had been expected, the deuterated radicals gave a well resolved ESR spectrum consisting of a 1:1:1 triplet of 1:3:3:1 quartets, showing that the quartet hyperfine splitting is certainly due to the anilino meta and phenylthiyl ortho protons. On the basis of the above result,

it can be said that the 2- and 6-phenyl groups give no hyperfine splitting (only broaden the line width).

When the ESR spectra of **4i** and **5i** were recording at a high gain (100 times the parent spectrum), satellite lines due to ^{33}S and ^{13}C at the natural abundance (^{33}S 0.76, ^{13}C 1.11%) could be observed in the both wings of the parent spectrum. From the spectrum $a_{^{33}S}$ and $a_{^{13}C}$ were determined to be 0.55 and 1.02 mT (**4i**) and 0.54 and 1.01 mT (**5i**), respectively. Assignments of the satellite lines observed were made by the intensity ratio of the satellite lines to the parent spectrum. The observed intensities are 0.12−0.13 (^{33}S) and 0.56−0.64% (^{13}C), which are in good agreement with the theoretical values (0.19% for ^{33}S and 0.56% for ^{13}C).

Isolation of 4, 5, and 6. As mentioned above, thioaminyls **4**, **5**, and **6** persist without decomposition. Temperature dependence of the ESR signal intensity for these radicals showed that the radicals exist in solution as individual radicals (and do not dimerize). We therefore decided to isolate thioaminyl radicals.

Isolation of **4**, **5**, and **6** was accomplished by the following procedures; a benzene solution of the corresponding precursors (**9**−**11**) was treated with PbO_2, and, after filtration, the solvent was removed by freeze-drying method. The resulting dark blue or dark green crystalline residue was crystallized from MeOH (**4c**, **4d**), EtOH−ethyl acetate (**4a**, **4b**, **4e**, **4f**, **4g**, **4h**, **5b**, **5c**, **5g**), hexane (**6c**), or hexanes−ethyl acetate (**6d**) to give dark blue or dark green needles or prisms in 16−52% yields.[13]

In the IR spectra no absorption peak due to the stretching vibration of the NH bond (3300−3370 cm^{-1}) was observed. The elemental analyses gave satisfactory agreements with the calculations. The radical purities determined by ESR using 3,4-dihydro-2,4,6-triphenyl-2*H*-1,2,4,5-tetrazin-1-yl (1,3,5-triphenylverdazyl)[14] as the reference was >95%. The magnetic susceptibility measurements of the radical crystals showed ~100% purities, as described below.

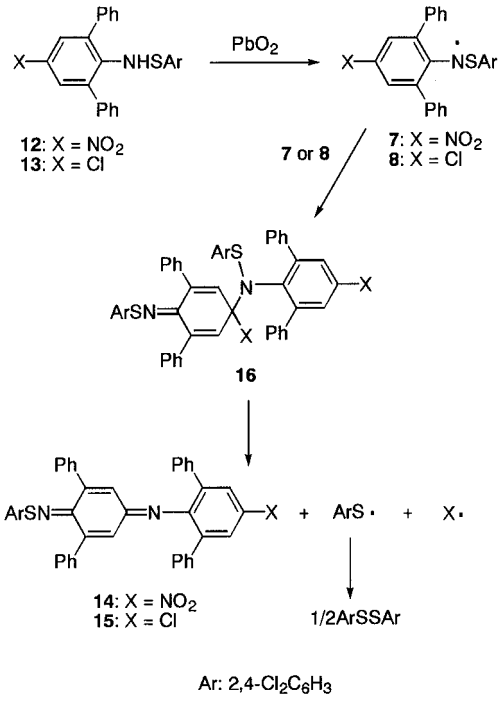
Product Analysis for Decomposition of 7 and 8. In contrast to **4**−**6**, radicals **7** and **8** are unstable, as mentioned above. To understand their decomposition mechanism, the product analysis for the decomposition was carried out. Radicals **7** and **8** were generated by oxidation of **12** or **13** with PbO_2 in benzene. After filtration, the resulting dark red mixture obtained was inspected by TLC. The TLC analyses showed formation of two main products (one is red and the other is colorless) and a few minor products, along with the unreacted precursor. The two main products, as well as the precursors, were isolated by column chromatograpy. The first eluted colorless product was identified as 2,4-dichlorophenyl disulfide on the basis of the IR and ^1H NMR spectra. The second eluted red products were the unknown compounds, and their structures were elucidated on the basis of the ^1H NMR, IR, and mass spectra. The ^1H NMR spectra were complex and relatively broad because there are many aromatic protons and the NMR samples were a mixture of syn- and anti-isomers as mentioned below. However, the ^1H NMR spectra clearly indicated that all peaks are in the aromatic region (6.22−8.28 for **14**, and 6.32−7.46 ppm for **15**) and suggested no peaks due to NH. No presence of NH was further confirmed by the IR spectra. The mass spectra gave a peak at *m/z* 707 (**14**) or 698 (**15**) as the molecular ion. The mass number 707 corresponds to 2 × **7** − (2,4-$Cl_2C_6H_3S$ + NO_2) and the mass number 698 corresponds to 2 × **8** − (2,4-$Cl_2C_6H_3S$ + Cl). On the basis of the above ^1H NMR, IR, and mass spectroscopic results, their structures were determined to be **14** and **15**, respectively. The elemental analyses also gave satisfactory results. Compounds **14** and **15** exist in solution as a mixture of *syn*- and anti-isomers. The results of the product analyses are summarized in Table 2.

Table 2. Product Analyses for Decomposition of 7 and 8

products from **7**[a]	yield[b]/%[c]	products from **8**[d]	yield[b]/%[c]
disulfide[e]	77	disulfide[e]	85
14	58	**15**	87

[a] 100 mg (0.214 mmol) of **12** was oxidized and 16 mg of unreacted **12** was recovered. [b] Yields after column chromatography. [c] Percent yields based on the reacted **12** or **13**. [d] 200 mg (0.438 mmol) of **13** was oxidized, and 91 mg of unreacted **13** was recovered. [e] 2,4-Dichlorophenyl disulfide.

Scheme 2



A plausible mechanism for the decomposition is shown in Scheme 2. The first step is the N−C coupling between two thioaminyl radicals to give **16**.[15] Elimination of a 2,4-dichlorophenylthiyl radical and X (X: NO_2, Cl) from **16** gives **14** or **15**, along with 2,4-diclorophenyl disulfide. Consequently, the instabilities of **7** and **8** can be ascribed to the insufficient protection of the para position by the NO_2 or Cl group which allows attack by another **7** or **8** radicals.

X-ray Crystallographic Analysis. Although most of the thioaminyl radical crystals obtained were microneedles or microprisms unsuitable for the X-ray crystal-

(13) Fortunately, pure radical crystals were successfully obtained even from the crude precursors of **9a**−**d** in 16−26% yields after recrystallization.

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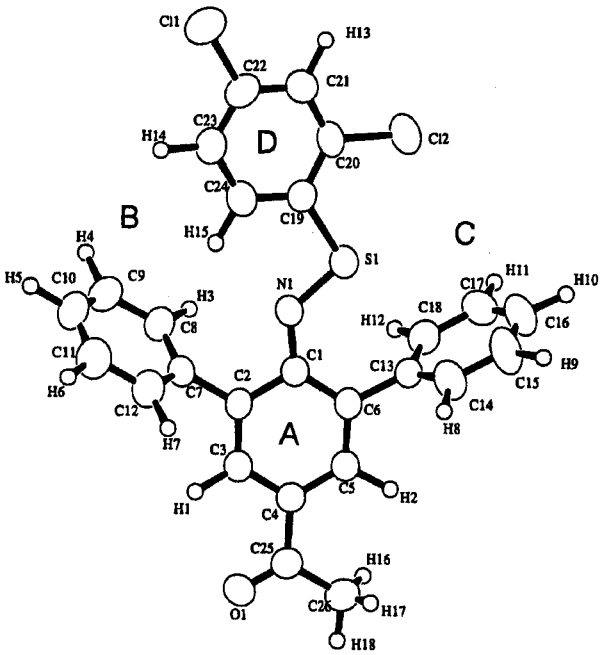


Figure 3. ORTEP drawing of **5c**.

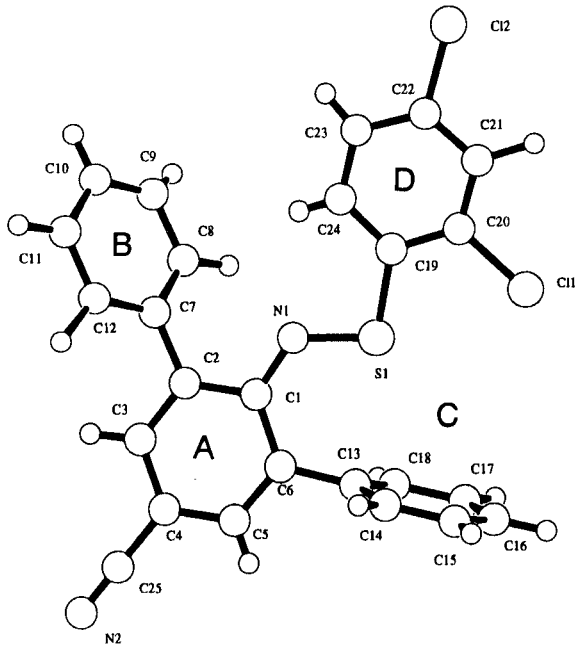


Figure 4. ORTEP drawing of **6c**.

lographic study, *N*-[(2,4-dichlorophenyl)thio]-4-acetyl-2,6-diphenylphenylaminyl (**5c**) and *N*-[(2,4-dichlorophenyl)-thio]-4-cyano-2,6-diphenylphenylaminyl (**6c**) gave sufficiently large prisms, allowing X-ray crystallographic analyses. The ORTEP drawings of **5c** and **6c** are illustrated in Figures 3 and 4, and the X-ray crystallographic data are shown in the Experimental Section. The selected bond lengths, bond angles, and torsion angles are summarized in Table 3.

The X-ray crystallographic studies for **5c** and **6c** gave the following structural features: In both radicals the benzene rings A and D and the N and S atoms (Ph−N−S−Ph plane) are almost in the same plane, as indicated by the torsion angles shown in Table 3. The carbonyl group is also planar to this coplane (the torsion angle of O1−C25−C4−C3 is −3.8°). On the other hand, the

Table 3. Selected Bond Lengths and Angles and Torsion Angles of 5c and 6c

5c

Bond Lengths (Å)		Bond Angles (deg)	
C1−N1	1.364(4)	C2−C1−N1	113.2(3)
N1−S1	1.619(3)	C6−C1−N1	128.1(3)
S1−C19	1.770(4)	C1−N1−S1	125.5(3)
		N1−S1−C19	98.7(2)

Torsion Angles (deg)			
S1−N1−C1−C2	178.4(3)	N1−S1−C19−C24	8.1(4)
S1−N1−C1−C6	0.4(6)	N1−S1−C19−C20	−172.2(3)
C1−N1−S1−C19	−179.1(3)	O1−C25−C4−C3	−3.8(6)

6c

Bond Lengths (Å)		Bond Angles (deg)	
C1−N1	1.341(7)	C2−C1−N1	115.1(5)
N1−S1	1.634(4)	C6−C1−N1	126.8(5)
S1−C19	1.767(6)	C1−N1−S1	123.7(4)
		N1−S1−C19	100.9(3)

Torsion Angles (deg)			
S1−N1−C1−C2	−177.4(4)	N1−S1−C19−C24	3.2(6)
S1−N1−C1−C6	6.7(9)	N1−S1−C19−C20	−177.0(5)
C1−N1−S1−C19	179.4(5)		

dihedral angle between the benzene rings A and B is 62.1 (**5c**) or 45.9° (**6c**), and that between the benzene rings A and C is 77.1 (**5c**) or 84.2° (**6c**), indicating that there are serious steric congestions around the nitrogen radical center surrounded by the two phenyl groups. Consequently, it can be concluded that the π-framework consisting of the A and D benzene rings and the N and S atoms is nearly planar, but the B and C benzene rings are significantly twisted from the coplane in both radicals. The X-ray crystallographic results are in good agreement with the ESR results which show that the unpaired electron is extensively delocalized onto the anilino benzene ring and phenylthiyl group.

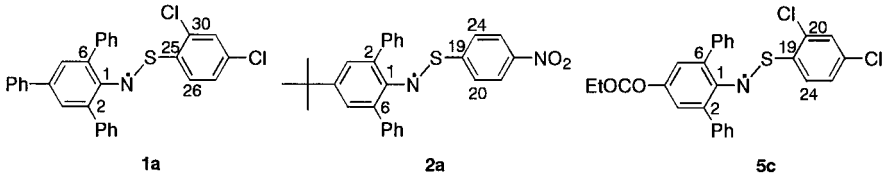
Upon comparison of the X-ray crystallographic data with **1**−**3**,[1,5] it is obvious that the bond lengths and bond angles are nearly identical, but the planarity of the Ph−N−S−Ph π-frameworks is somewhat different from those for **1**−**3**. As shown by the C−C−N−S, C−N−S−C, and N−S−C−C torsion angles (Table 4), **5c** and **6c** have the most planar π-frameworks, and **2** and **3** have the less planar π-frameworks. Consequently, the planarity of the Ph−N−S−Ph π-framework is in the order **4** ≈ **5** > **1** > **2** ≈ **3**.

UV−vis Spectra of Thioaminyl Radicals. Aminyls **4**, **5**, and **6** are characterized by a blue (**4a**,**c**−**e**,**g**−**h**, **6**) or green color (**4b**,**f**, **5**) in solution. The UV−vis spectra of **4f** and the corresponding precursor, **9f**, are shown in Figure 5. The UV−vis spectral data for **4**−**6** are summarized in Table 5.

Aminyl **4f** shows absorption peaks at 627 (ϵ 5420), 473 (6790), 412 (19000), and 307 nm (10000), while **5f** absorbs only at 337 nm (ϵ 13800). Since any precursor has no strong absorption in the visible region, the radical concentrations can be easily determined by the characteristic absorptions in the visible region.

Spin Density Distribution. To discuss quantitatively the spin density distribution in the present radicals, MO calculations for **5** were performed by the McLachlan-perturbation method using the following parameters: $\alpha_N = \alpha + 0.6\beta$, $\alpha_S = \alpha + \beta$, $\alpha_O = \alpha + 2.0\beta$, $\alpha_{C25} = \alpha + 0.1\beta$, $\beta_{CN} = 1.1\beta$, $\beta_{NS} = 0.7\beta$, $\beta_{CS} = 0.7\beta$, β_{C4-C25}

Table 4. Comparison of Torsion Angles of 5c with 1a and 2a[a]



1a **2a** **5c**

1a		2a		5c	
C2−C1−N−S	−170.4	C2−C1−N−S	22.4	C2−C1−N−S	178.4
C6−C1−N−S	14.6	C6−C1−N−S	−158.1	C6−C1−N−S	0.4
C1−N−S−C25	−174.7	C1−N−S−C19	175.3	C1−N−S−C19	−179.1
N−S−C25−C26	2.2	N−S−C19−C20	2.4	N−S−C19−C24	8.1
N−S−C25−C30	179.8	N−S−C19−C24	−178.7	N−S−C19−C20	−172.2

[a] The torsion angles are given in degrees.

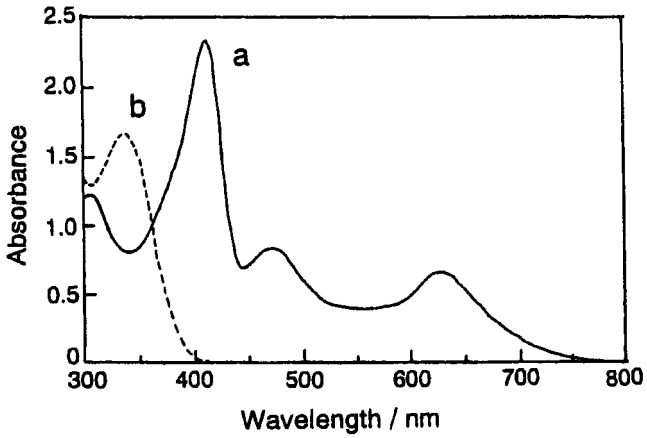


Figure 5. UV-vis spectra of **4b** and **9b** in benzene: (a) **4b**, 0.123 mM; (b) **9b**, 1.22 mM.

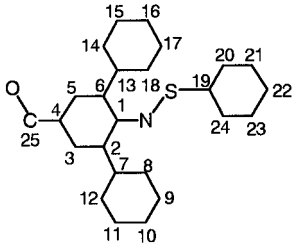
Table 5. UV−Vis Spectral Data of 4, 5, and 6 in Benzene

radical	λ_{max}/nm (ϵ/L mol^{-1} cm^{-1})
4a	372 (14500), 408 (10600 sh), 546 (3030sh), 617 (4820)
4b	311 (10200), 413 (19100), 480 (7610), 623 (5340)
4c	306 (6190 sh), 383 (18500), 559 (4010 sh), 634 (6430)
4d	381 (17400), 554 (3290 sh), 618 (5190)
4e	374 (14500), 545 (3190 sh), 621 (5000)
4f	307 (10000), 412 (19000), 473 (6790), 627 (5420)
4g	308 (5820 sh), 383 (17200), 426 (6930 sh), 640 (5980)
4h	381 (19100), 556 (3710 sh), 623 (5720)
5b	313 (8830), 425 (20100), 477 (6310), 633 (4980)
5c	315 (6360 sh), 390 (16800), 437 (10700), 554 (3190 sh), 644 (6160)
5g	389 (14500), 439 (8310), 550 (2550 sh), 650 (5140)
6c	381 (12100), 425 (4040 sh), 554 (2560 sh), 644 (4470)
6d	313 (4330 sh), 378 (14000), 543 (2600 sh), 628 (4540)

$= 0.7\beta$, $\beta_{C25-O} = 1.37\beta$, and $\lambda = 0.7$.[1,5,16] The resonance integrals between C2−C7 and C6−C13 are changed to 0.22β ($= \cos^2 62.9°$) and 0.05β ($= \cos^2 77.1°$), respectively, on the basis of the X-ray crystallographic results of **5c**. The results of the calculations are listed in Table 6.

As found in Table 6, the calculations are in good agreement with the experimental results, and the following conclusions are withdrawn from Table 6. First, the unpaired electron is extensively delocalized over the anilino and phenylthiyl groups. Second, a small amount of the spin densities appears on the acetyl group. Third, the delocalization of the unpaired electron onto the 2- and 6-phenyl groups is negligibly small due to the significant twisting. Although delocalization of the unpaired electron onto the carbonyl group cannot be experimentally confirmed until the carbonyl carbon or oxygen is labeled by ^{13}C or ^{17}O, a small delocalization of the unpaired electron onto the cyano group is observed in the ESR spectra of **6**, as mentioned above.

Table 6. Experimental and Calculated Hyperfine Coupling Constants for 5



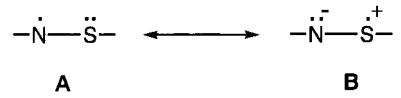
position	obsd hfc const[a]	calcd spin density	calcd hfc const[a,b]
N	0.876	0.405	0.891
S	0.55[c]	0.211	0.485
1		−0.035	
2		0.118	
3	0.132[d]	−0.023	0.062[d]
4		0.106	
5	0.132[d]	−0.023	0.062[d]
6		0.119	
7		−0.001	
8, 12		0.001	
9, 11		−0.000	
10		0.001	
13		−0.000	
14, 18		0.000	
15, 17		−0.000	
16		0.000	
19		−0.012	
20, 24	0.097[d]	0.026	−0.070[d]
21, 23		−0.008	
22	0.097[d,e]	0.024	−0.065[d]
25		0.051	
O		0.022	

[a] The hyperfine coupling constants are given in mT. [b] Derived from the hfc constants using the equation, $a_X = Q_X\rho_X$, where $Q_H = -2.7$, $Q_N = 2.2$, and $Q^{33}_S = 2.3$ mT. [c] The value for **5i**. [d] The hfc constant for the proton attached to the carbon. [e] The value for **5g**.

Comparison of ESR Parameters with Structurally Related Radicals. Thioaminyls **4**−**6** are structurally close to **1**−**3**.[5−7] The hyperfine coupling constants and *g* values for **4**−**6** are compared with those for **1**−**3** and **17** in Table 7. Radical **17** is a structurally basic radical for **1**−**8**.[17] Although there are no large differences in the hfc constants and *g* values between **4**−**6** and **1**−**3**

(16) Miura, Y.; Asada, H.; Kinoshita, M.; Ohta, K. *J. Phys. Chem.* **1983**, *87*, 3450.

Scheme 3



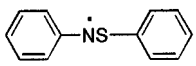
A B

Table 7. Comparison of the ESR Parameters of 4−6 with Structurally Related Thioaminyl Radicals

radical	a_N	a_H[b]	a^{33}_S	g
1	0.890−0.896	0.133−0.134	0.51	2.0054−2.0059
2	0.921−0.936	0.126−0.130	0.51	2.0054−2.0060
3	0.932−0.953	0.127−0.138		2.0054−2.0058
17	0.959	0.126		2.0059
4	0.886−0.893	0.125−0.133	0.55	2.0059−2.0061
5	0.876−0.881	0.132	0.54	2.0060−2.0062
6	0.875−0.876	0.128−0.130		2.0057−2.0060

[a] The hfc constants are given in mT. [b] The hfc constants due to the anilino meta protons.

and **17**, there are some small differences. First, the a_N values for **4**−**6** are somewhat smaller than those for **1**−**3**



17

and **17**. Second, the a^{33}_S values for **4**−**6** are 0.03−0.04 mT larger than those for **1** and **2**. Thioaminyl radicals **4**−**6**, as well as **1**−**3** and **17**, can be well represented by the canonical structures A and B (Scheme 3). If the relative importance of A is reduced and the relative importance of B is enhanced, a_N values will be reduced and a^{33}_S will be increased, with an increase in the g values.[18] Since **4**−**6** bear an electron-withdrawing substituent at the para position of the anilino group, the relative importance of canonical structure B will be increased. The reduction in a_N and increases in a^{33}_S and g can therefore be accounted for in terms of an increase in the relative importance of canonical structure B.

Magnetic Susceptibility Measurements. The magnetic susceptibility (χ) measurements were carried out for five thioaminyl radicals using polycrystalline samples with a SQUID magnetometer in the temperature range 1.8−300 K. The diamagnetic components were subtracted by the estimation based on Pascal's sum rule for the atomic contribution and the structural correction. The purities of the radicals used were shown to be ~100% by the magnetic susceptibility measurements.

Figure 6 shows $\chi_{mol}T$ vs T plots for **4f** (χ_{mol}: molar magnetic susceptibility). Although $\chi_{mol}T$ is constant above 100 K, it sharply increases below 100 K with the lowering of temperature, indicating the spin-exchange interaction between the unpaired electron spins is ferromagnetic. The magnetic behavior was analyzed in terms of the regular one-dimensional Heisenberg model[19] (eq 1) with $2J/k_B = 16.0$ K.

$$H = -2J\sum S_i S_j \qquad (1)$$

In contrast, **6c** showed a strong antiferomagnetic coupling between the unpaired electron spins. As found in Figure 7, $\chi_{mol}T$ is already reduced at room temperature and, with lowering of temperature, drastically reduced.

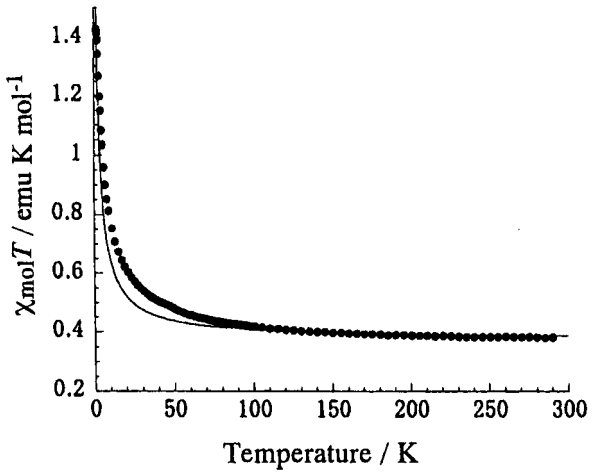


Figure 6. χT vs T plots of **4f**.

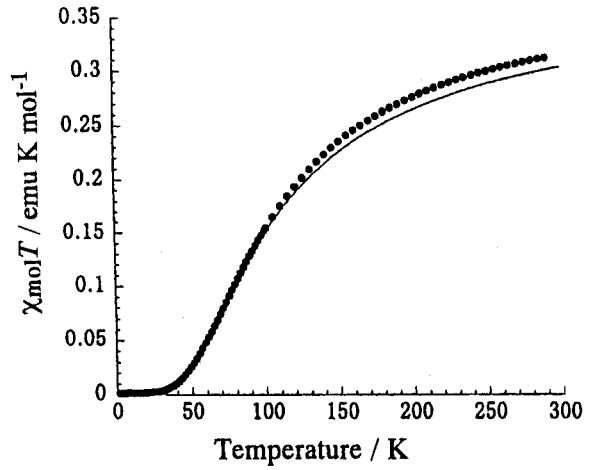


Figure 7. χT vs T plots of **6c**.

The observed $\chi_{mol}T$ vs T plots were analyzed in terms of the alternating linear chain model (eq 2)[20] with $2J/k_B = -194.6$ K and $\alpha = 0.09$. An origin of the strong antiferromagnetic interaction can be found in its crystal structure which indicates that **6c** forms a dimer having a large SOMO−SOMO overlap in the radical crystal.

$$H = -2J\sum[S_{2i}S_{2i} + \alpha S_{2i}S_{2i+1}] \qquad (2)$$

In the cases of **4h**, **5c**, and **5g** the magnetic exchange interactions were also antiferromagnetic. The $\chi_{mol}T$ vs T plots for **5c** were analyzed with the singlet−triplet model with $2J/k_B = -15.6$ K, and for **4h** and **5g** the magnitudes of the magnetic exchange interactions were estimated by the Weiss temperature θ obtained from the $1/\chi_{mol}$ vs T plots because the magnetic exchange interactions are very weak (**4h**, −5.0 K; **5g**, −0.6 K).

Conclusions. In the present study 4-ethoxycarbonyl (**4**), 4-acetyl (**5**), 4-cyano (**6**), 4-nitro (**7**), and 4-chloro (**8**) substituted *N*-(arylthio)-2,6-diarylphenylaminyl radicals were prepared. Although the 4-nitro and 4-chloro substituted radicals are unstable and immediately decompose, 4-ethoxycarbonyl, 4-acetyl, and 4-cyano substituted radicals are very stable and could be isolated as

(17) Miura, Y.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1142.
(18) The spin−orbit coupling parameter is 382 cm^{-1}; McClure, D. S. *J. Chem. Phys.* **1949**, *17*, 905.
(19) Bonner, J. C.; Fisher, M. E. *Phys. Rev.* **1964**, *A135*, 640.
(20) (a) Duffy, W., Jr.; Barry, K. P. *Phys. Rev.* **1968**, *165*, 647. (b) Hall, J. W.; March, W.; Weller, R. R.; Hatfield, W. E. *Inorg. Chem.* **1981**, *20*, 1033.

pure radical crystals. The product analyses for the decomposition of the 4-nitro and 4-chloro substituted radicals indicated that the decomposition proceeds via formation of the C−N coupled dimer. The X-ray crystallographic analyses for **5c** and **6c** exhibited that the Ph−N−S−Ph framework is nearly planar, while the 2- and 6-phenyl groups are significantly twisted from the coplane. The ESR results for the thioaminyl radicals indicated that the unpaired electron is extensively delocalized over the anilino and phenylthiyl benzene rings. The magnetic susceptibility measurements showed that, although four radicals couple antiferromagnetically with $2J/k_B = -15.6$ to -194.6 K or $\theta = -0.6$ to -5.0 K, one radical couples ferromagnetically with $2J/k_B = +16.0$ K. The detailed magnetic behavior of the ferromagnetic radical in the low-temperature region below 2 K is now under investigation.

Experimental Section

Preparative GPC separation was performed with a LC-908 recycling preparative HPLC instrument (Japan Analytical Industry Co. LTD). IR spectra were run on a JASCO FT/IR-230 spectrophotometer. UV−vis spectra were measured with a Shimadzu UV-2200 spectrophotometer. ^{1}H NMR spectra,[21] mass spectra,[21] and ESR spectra[1] were taken as previously reported. Magnetic susceptibility measurements were performed in the temperature range 1.8−300 K on a Quantam-Design MPMS2 SQUID magnetometer. Diamagnetic contributions were estimated by Pascal's sum rule.

4-(Ethoxycarbonyl)aniline, 4-acetylaniline, 4-cyanoaniline, 4-chloroaniline, and 2,6-dibromo-4-nitroaniline were commercially available. Phenylboronic acid, 4-chlorophenylboronic acid, and phenylboronic-d_5 acid were obtained according to the reported methods.[1] 4-(Ethoxycarbonyl)-2,6-dibromoaniline, 4-acetyl-2,6-dibromoaniline, 2,6-dibromo-4-cyanoaniline, and 4-chloro-2,6-dibromoaniline were obtained by treating 40 mmol of the anilines with 39.0 g (100 mmol) of benzyltrimethylammonium tribromide (BTMA·Br_3) in CH_2Cl_2 (400 mL)−MeOH (160 mL) at room temperature for 3 h in the presence of 11.2 g of $CaCO_3$ in the usual manner.[10] Crystallization gave 4-(ethoxycarbonyl)-2,6-dibromoaniline as colorless needles (EtOH) with mp 107−108 °C in 80% yield, 4-acetyl-2,6-dibromoaniline as colorless fine prisms (EtOH) with mp 168−169 °C in 83% yield, 4-cyano-2,6-dibromoaniline as colorless needles (EtOH) with mp 121−122 °C in 81% yield, and 4-chloro-2,6-dibromoaniline as colorless needles (hexane) with mp 93−95 °C in 93% yield, respectively. Silica gel column chromatography was carried out on Wako gel C-200, and alumina column chromatography on Merck aluminum oxide 90.

A General Procedure for Preparation of 4-Substituted 2,6-Diarylanilines. A mixture of 20 mmol of 4-substituted (ethoxycarbonyl, acetyl, cyano, nitro, and chloro) 2,6-dibromoaniline, 60 mmol of arylboronic acid, 2.78 g (2.41 mmol) of $(PPh_3)_4Pd$, 17.0 g of Na_2CO_3 in benzene (200)−EtOH (30)−water (80 mL) (for 4-(ethoxycarbonyl)-, 4-acetyl-, 4-cyano-, and 4-chloro-2,6-dibromoanilines) or in dimethoxyethane (300)−EtOH (30)−water (80 mL) (for 4-nitro-2,6-dibromoaniline) was refluxed for 14 h under a nitrogen atmosphere.[11] The organic layer was extracted with benzene or $CHCl_3$, and the combined extracts were washed with brine. After drying ($MgSO_4$), the solvent was evaporated and the residue chromatographed on silica gel with benzene (4-(ethoxycarbonyl)-2,6-diarylaniline, 4-nitro-2,6-diphenylaniline), 1:10 ethyl acetate−benzene (4-acetyl-2,6-diarylaniline), or 1:3 benzene−hexane (4-chloro-2,6-diphenylaniline), or on alumina with CH_2Cl_2 (4-cyano-2,6-diphenylaniline). Crystallization from the appropriate solvents gave pure 4-substituted 2,6-diarylanilines.

(21) Miura, Y.; Oka, H.; Yamano, E.; Morita, M. *J. Org. Chem.* **1997**, *62*, 1188.

4-(Ethoxycarbonyl)-2,6-diphenylaniline: colorless needles (hexane); yield 90%; mp 96−97 °C; IR (KBr) 3470 and 3360 (NH_2) and 1700 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.35 (t, J = 7.3 Hz, 3 H), 4.26 (s, 2 H), 4.32 (q, J = 7.3 Hz, 2 H), 7.36−7.51 (m, 10 H), 7.83 (s, 2 H). Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41. Found: 79.41; H, 6.08; N, 4.37.

4-(Ethoxycarbonyl)-2,6-bis(4-chlorophenyl)aniline: colorless needles (EtOH); yield 87%; mp 155−156 °C; IR (KBr) 3470 and 3380 (NH_2) and 1720 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.35 (t, J = 7.3 Hz, 3 H), 4.18 (s, 2 H), 4.33 (q, J = 7.3 Hz, 2 H), 7.41−7.47 (m, 8 H), 7.79 (s, 2 H). Anal. Calcd for $C_{21}H_{17}Cl_2NO_2$: C, 65.30; H, 4.44; N, 3.63. Found: C, 65.17; H, 4.49; N, 3.61.

4-(Ethoxycarbonyl)-2,6-di(phenyl-d_5)aniline: colorless needles (hexane); yield 88%; mp 98−99 °C; IR (KBr) 3470 and 3380 (NH), 1700 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.35 (t, J = 7.3 Hz, 3 H), 4.18 (s, 2 H), 4.33 (q, J = 7.3 Hz, 2 H), 7.83 (s, 2 H).

4-Acetyl-2,6-diphenylaniline: colorless prisms (hexanes−EtOH); yield 72%; mp 138−139 °C; IR (KBr) 3470 and 3370 (NH_2) and 1660 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.53 (s, 3 H), 4.35 (s, 2 H), 7.35−7.49 (m, 10 H), 7.76 (s, 2 H). Anal. Calcd for $C_{20}H_{17}NO$: C, 83.59; H, 5.96; N, 4.88. Found: 83.44; H, 5.96; N, 4.80.

4-Acetyl-2,6-bis(4-chlorophenyl)aniline: colorless prisms (EtOH-ethyl acetate); yield 60%; mp 203−204 °C; IR (KBr) 3460 and 3350 (NH_2) and 1660 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.53 (s, 3 H), 4.25 (s, 2 H), 7.42 (d, J = 8.8 Hz, 4 H), 7.47 (d, J = 8.8 Hz, 4 H), 7.76 (s, 2 H). Anal. Calcd for $C_{20}H_{15}Cl_2NO$: C, 67.43; H, 4.24; N, 3.93. Found: C, 67.49; H, 4.29; N, 3.91.

4-Acetyl-2,6-di(phenyl-d_5)aniline: colorless prisms (hexanes−EtOH); yield 67%; mp 140−141 °C; IR (KBr) 3470 and 3370 (NH_2), 1660 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.54 (s, 3 H); 4.27 (s, 2 H), 7.77 (s, 2 H).

4-Cyano-2,6-diphenylaniline: light yellow prisms (EtOH); yield 80%; mp 152−154 °C; IR (KBr) 3480 and 3390 (NH_2), 2210 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 4.35 (s, 2H), 7.38 (s, 2 H), 7.40−7.51 (m, 10 H). Anal. Calcd for $C_{19}H_{14}N_2$: C, 84.41; H, 5.23; N, 10.36. Found: C, 84.39; H, 5.12; N, 10.32.

4-Nitro-2,6-diphenylaniline: light yellow plates (hexane−benzene); yield 95% yield; mp 167−168 °C; IR (KBr) 3480 and 3380 cm^{-1} (NH_2); ^{1}H NMR ($CDCl_3$) δ 4.59 (s, 2 H), 7.41−7.53 (m, 10 H), 8.05 (s, 2 H). Anal. Calcd for $C_{18}H_{14}N_2O_2$: C, 74.46; H, 4.86; N, 9.65. Found: C, 74.78; H, 4.89; N, 9.58.

4-Chloro-2,6-diphenylaniline: colorless prisms (hexane); yield 73%; mp 79−81 °C; IR (KBr) 3460 and 3350 cm^{-1} (NH_2); ^{1}H NMR ($CDCl_3$) δ 3.81 (s, 2H), 7.11 (s, 2 H), 7.46−7.50 (m, 10 H). Anal. Calcd for $C_{18}H_{14}ClN$: C, 77.27; H, 5.05; N, 5.01. Found: C, 77.28; H, 4.95; N, 4.96.

General Procedure for Preparation of 9−13. To a stirred solution of 6.30 mmol of 4-substituted 2,6-diarylanilines and 1.46 g (2.0 mL) of Et_3N in 200 mL of dry ether (or anhydrous THF) was added at 0 °C a solution of 7.8 mmol of arenesulfenyl chloride in 20 mL of dry ether (or anhydrous THF). After being stirred for 2 h at 0 °C, the mixture was filtered and evaporated under reduced pressure, and the residue was chromatographed on alumina with benzene (**10b**, **10c**, **10g**, **10i**), 2:1 (**9e** and **9f**), 1:1 (**9a**−**d**, **9g**−**i**, **11c**, **11d**, **12**), or 1: 5 benzene−hexane (**13**) as eluant. Compounds **9a**−**d** were used in the following oxidation step without further purification. The analytical samples of **9a**−**d** were obtained by separation of almost pure parts with a preparative GPC instrument using $CHCl_3$ as eluant and subsequent recrystallization from MeOH. The other compounds were purified by recrystallization.

***N*-[(3-Nitrophenyl)thio]-4-(ethoxycarbonyl)-2,6-diphenylaniline (9a):** light yellow fine prisms (MeOH); yield 43%; mp 47−49 °C; IR (KBr) 3330 (NH), 1720 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.35 (t, J = 7.3 Hz, 3 H), 4.34 (q, J = 7.3 Hz, 2 H), 5.65 (s, 1 H), 7.02 (d, J = 8.3 Hz, 1 H), 7.21 (t, J = 8.3 Hz, 1 H), 7.32−7.40 (m, 10 H), 7.63 (t, J = 2.0 Hz, 1 H),

7.84 (dd, J = 8.3 and 2.0 Hz, 1 H), 7.85 (s, 2 H). Anal. Calcd for $C_{27}H_{22}N_2O_4S$: C, 68.92; H, 4.71; N, 5.95. Found: C, 69.45; H, 4.92; N, 5.58.

***N*-[(4-Nitrophenyl)thio]-4-(ethoxycarbonyl)-2,6-diphenylaniline (9b):** light yellow fine prisms (MeOH); yield 46%; mp 61−62 °C; IR (KBr) 3300 (NH), 1710 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$) δ 1.35 (t, J = 7.3 Hz, 3 H), 4.34 (q, J = 7.3 Hz, 2 H), 5.65 (s, 1 H), 6.85 (d, J = 9.0 Hz, 2 H), 7.28−7.41 (m, 10 H), 7.87 (s, 2 H), 7.90 (d, J = 9.0 Hz, 2 H). Anal. Calcd for $C_{27}H_{22}N_2O_4S$: C, 68.92; H, 4.71; N, 5.95. Found: C, 69.15; H, 4.81; N, 5.74.

***N*-[(2,4-Dichlorophenyl)thio]-4-(ethoxycarbonyl)-2,6-diphenylaniline (9c):** colorless fine prisms (MeOH); yield 34%; mp 119−120 °C; IR (KBr) 3360 (NH), 1690 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$) δ 1.35 (t, J = 7.3 Hz, 3 H), 4.34 (q, J = 7.3 Hz, 2 H), 5.51 (s, 1 H), 6.86 (d, J = 8.8 Hz, 1 H), 6.98 (dd, J = 8.8 and 2.0 Hz, 1 H), 7.08 (d, J = 2.0 Hz, 1 H), 7.30−7.36 (m, 10 H), 7.85 (s, 2 H). Calcd for $C_{27}H_{21}Cl_2NO_2S$: C, 65.59; H, 4.28; N, 2.83. Found: C, 65.41; H, 4.33; N, 2.81.

***N*-[(3,5-Dichlorophenyl)thio]-4-(ethoxycarbonyl)-2,6-diphenylaniline (9d):** colorless fine prisms (MeOH); yield 27%; mp 43−45 °C; IR (KBr) 3340 (NH), 1720 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$) δ 1.35 (t, J = 7.3 Hz, 3 H), 4.34 (q, J = 7.3 Hz, 2 H), 5.61 (s, 1 H), 6.60 (d, J = 2.0 Hz, 2 H), 6.99 (t, J = 2.0 Hz, 1 H), 7.31−7.42 (m, 10 H), 7.86 (s, 2 H). Anal. Calcd for $C_{27}H_{21}Cl_2NO_2S$: C, 65.59; H, 4.28; N, 2.83. Found: C, 65.27; H, 4.31; N, 2.80.

***N*-[(3-Nitrophenyl)thio]-4-(ethoxycarbonyl)-2,6-bis(4-chlorophenyl)aniline (9e):** light yellow fine prisms (EtOH); yield 26%; mp 64−65 °C; IR (KBr) 3330 (NH), 1710 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$) δ 1.35 (t, J = 7.3 Hz, 3 H), 4.35 (q, J = 7.3 Hz, 2 H), 5.51 (s, 1 H), 7.05 (d, J = 8.3 Hz, 1 H), 7.27 (t, J = 8.3 Hz, 1 H), 7.29 (s, 8 H), 7.65 (t, J = 2.0 Hz, 1 H), 7.83 (s, 2 H), 7.93 (d, J = 8.3 Hz, 1 H). Anal. Calcd for $C_{27}H_{20}Cl_2N_2O_4S$: C, 60.12; H, 3.74; N, 5.19. Found: C, 59.81; H, 3.77; N, 5.10.

***N*-[(4-Nitrophenyl)thio]-4-(ethoxycarbonyl)-2,6-bis(4-chlorophenyl)aniline (9f):** light yellow needles (EtOH−benzene); yield 54%; mp 144−145 °C; IR (KBr) 3330 (NH), 1710 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$) δ 1.36 (t, J = 7.3 Hz, 3 H), 4.35 (q, J = 7.3 Hz, 2 H), 5.49 (s, 1 H), 6.88 (d, J = 9.0 Hz, 2 H), 7.30 (s, 8 H), 7.84 (s, 2 H), 7.96 (d, J = 9.0 Hz, 2 H). Anal. Calcd for $C_{27}H_{20}Cl_2N_2O_4S$: C, 60.12; H, 3.74; N, 5.19. Found: C, 59.63; H, 3.71; N, 5.07.

***N*-[(2,4-Dichlorophenyl)thio]-4-(ethoxycarbonyl)-2,6-bis(4-chlorophenyl)aniline (9g):** colorless needles (EtOH); yield 51%; mp 144−145 °C; IR (KBr) 3300 (NH), 1710 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$) δ 1.35 (t, J = 7.3 Hz, 3 H), 4.34 (q, J = 7.3 Hz, 2 H), 5.35 (s, 1H), 6.86 (d, J = 8.3 Hz, 1 H), 7.02 (dd, J = 8.3 and 2.0 Hz, 1 H), 7.15 (d, J = 2.0 Hz, 1 H), 7.25−7.32 (m, 8 H), 7.81 (S, 2 H). Anal. Calcd for $C_{27}H_{19}Cl_4NO_2S$: C, 57.57; H, 3.40; N, 2.49. Found: C, 57.53; H, 3.42; N, 2.48.

***N*-[(3,5-Dichlorophenyl)thio]-4-(ethoxycarbonyl)-2,6-bis(4-chlorophenyl)aniline (9h):** colorless needles (EtOH); yield 48%; mp 159−161 °C; IR (KBr) 3330 (NH), 1710 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$) δ 1.36 (t, J = 7.3 Hz, 3 H), 4.35 (q, J = 7.3 Hz, 2 H), 5.45 (s, 1 H), 6.63 (d, J = 1.5 Hz, 2 H), 7.06 (t, J = 1.5 Hz, 1 H), 7.29−7.38 (m, 8 H), 7.83 (S, 2 H). Anal. Calcd for $C_{27}H_{19}Cl_4NO_2S$: C, 57.57; H, 3.40; N, 2.49. Found: C, 57.56; H, 3.46; N, 2.47.

***N*-[(2,4-Dichlorophenyl)thio]-4-(ethoxycarbonyl)-2,6-di(phenyl-d_5)aniline (9i):** colorless fine plates (MeOH); yield 44%; mp 123−124 °C; IR (KBr) 3370 (NH), 1690 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$) δ 1.35 (t, J = 7.3 Hz, 3 H), 4.34 (q, J = 7.3 Hz, 2 H), 5.52 (s, 1 H), 6.86 (d, J = 8.8 Hz, 1 H), 6.98 (dd, J = 8.8 and 2.0 Hz, 1 H), 7.08 (d, J = 2.0 Hz, 1 H), 7.85 (s, 2 H). Calcd for $C_{27}H_{11}D_{10}Cl_2NO_2S$: C, 64.28; H, 4.20; N, 2.78. Found: C, 64.20; H, 4.35; N, 2.70.

***N*-[(4-Nitrophenyl)thio]-4-acetyl-2,6-diphenylaniline (10b):** light yellow fine prisms (EtOH−benzene); yield 48%; mp 150−151 °C; IR (KBr) 3320 (NH), 1670 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$) δ 2.56 (s, 3 H), 5.67 (s, 1 H), 6.85 (d, J = 8.8 Hz, 2 H), 7.31−7.41 (m, 10 H), 7.79 (s, 2 H), 7.91 (d, J = 8.8 Hz, 2 H). Anal. Calcd for $C_{26}H_{20}N_2O_3S$: C, 70.89; H, 4.58; N, 6.36. Found: C, 70.87; H, 4.61; N, 6.33.

***N*-[(2,4-Dichlorophenyl)thio]-4-acetyl-2,6-diphenylaniline (10c):** colorless fine prisms (EtOH−benzene); yield 56%; mp 131−132 °C; IR (KBr) 3320 (NH), 1680 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$) δ 2.56 (s, 3 H), 5.55 (s, 1 H), 6.86 (d, J = 8.3 Hz, 1 H), 7.00 (dd, J = 8.3 and 2.0 Hz, 1 H), 7.08 (d, J = 2.0 Hz, 1 H), 7.32−7.36 (m, 10 H), 7.77 (s, 2 H). Anal. Calcd for $C_{26}H_{19}Cl_2NOS$: C, 67.24; H, 4.12; N, 3.02. Found: C, 67.32; H, 4.16; N, 3.00.

***N*-[(2,4-Dichlorophenyl)thio]-4-acetyl-2,6-bis(4-chlorophenyl)aniline (10g):** colorless prisms (EtOH−benzene); yield 51%; mp 158−159 °C; IR (KBr) 3290 (NH), 1680 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$) δ 2.56 (s, 3 H), 5.38 (s, 1H), 6.86 (d, J = 8.3 Hz, 1 H), 7.03 (dd, J = 8.3 and 2.0 Hz, 1 H), 7.15 (d, J = 2.0 Hz, 1 H), 7.25−7.33 (m, 8 H), 7.74 (S, 2 H). Anal. Calcd for $C_{26}H_{17}Cl_4NOS$: C, 58.55; H, 3.22; N, 2.63. Found: C, 58.64; H, 3.30; N, 2.60.

***N*-[(2,4-Dichlorophenyl)thio]-4-acetyl-2,6-di(phenyl-d_5)aniline (10i):** colorless plates (EtOH−benzene); yield 56%; mp 136−137 °C; IR (KBr) 3290 (NH), 1680 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$) δ 2.56 (s, 3 H), 5.55 (s, 1 H), 6.86 (d, J = 8.3 Hz, 1 H), 6.99 (dd, J = 8.3 and 2.0 Hz, 1 H), 7.08 (d, J = 2.0 Hz, 1 H), 7.77 (s, 2 H). Anal. Calcd for $C_{26}H_9Cl_2D_{10}NOS$: C, 65.82; H, 4.04; N, 2.95. Found: C, 65.85; H, 4.10: N, 2.93.

***N*-[(2,4-Dichlorophenyl)thio]-4-cyano-2,6-diphenylaniline (11c):** colorless needles (EtOH−benzene); yield 54%; mp 128−129 °C; IR (KBr) 3340 (NH), 2230 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 5.55 (s, 1 H), 6.84 (d, J = 8.3 Hz, 1 H), 7.01 (dd, J = 8.3 and 2.0 Hz, 1 H), 7.10 (d, J = 2.0 Hz, 1 H), 7.32−7.38 (m, 10 H), 7.44 (s, 2 H). Anal. Calcd for $C_{25}H_{16}Cl_2N_2S$: C, 67.11; H, 3.61; N, 6.26. Found: C, 67.03; H, 3.45: N, 6.22.

***N*-[(3,5-Dichlorophenyl)thio]-4-cyano-2,6-diphenylaniline (11d):** light blue prisms (EtOH); yield 90%; mp 131−133 °C; IR (KBr) 3260 (NH), 2240 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 5.64 (s, 1 H), 6.58 (d, J = 1.9 Hz, 2 H), 7.18 (t, J = 1.9 Hz, 1 H), 7.34−7.50 (m, 12 H). Anal. Calcd for $C_{25}H_{16}Cl_2N_2S$: C, 67.11; H, 3.61; N, 6.22. Found: C, 66.91; H, 3.48: N, 6.26.

***N*-(2,4-Dichlorophenyl)thio]-4-nitro-2,6-diphenylaniline (12):** light red needles (EtOH); yield 8%; mp 104−105 °C; IR (KBr) 3320 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ 5.69 (s, 1 H), 6.85 (d, J = 8.3 Hz, 1 H), 7.02 (dd, J = 8.3 and 2.0 Hz, 1 H), 7.11 (d, J = 2.0 Hz, 1 H), 7.34−7.42 (m, 10 H), 8.05 (s, 2 H). Anal. Calcd for $C_{24}H_{16}Cl_2N_2O_2S$: C, 61.68; H, 3.45; N, 5.99. Found: C, 61.76; H, 3.48; N, 5.96.

***N*-(2,4-Dichlorophenyl)thio]-4-chloro-2,6-diphenylaniline (13):** colorless prisms (hexane); yield 55%; mp 98−99 °C (dec); IR (KBr) 3340 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ 5.20 (s, 1 H), 6.84 (d, J = 8.3 Hz, 1 H), 6.95 (dd, J = 8.3 and 2.0 Hz, 1 H), 7.06 (d, J = 2.0 Hz, 1 H), 7.16 (s, 2 H), 7.28−7.33 (m, 10 H). Anal. Calcd for $C_{24}H_{16}Cl_3NS$: C, 63.10; H, 3.54; N, 3.07. Found: C, 63.15; H, 3.43; N, 3.07.

Isolation of 4, 5, and 6. Precursor **7**, **8**, or **11** (100 mg) was dissolved in 20 mL of benzene with stirring. After 1.0 g of K_2CO_3 was added, PbO_2 (1.0−1.2 g) was added to the vigrously stirred mixture in some portions during 2 min. After addition, stirring was continued for further 0.5−1.0 min, and the strongly colored reaction mixture was filtered. The solvent was removed by freeze-drying, and the resulting dark blue or green crystalline powder was crystallized from MeOH (**4c**, **4d**), EtOH−ethyl acetate (**4a**, **4b**, **4e**, **4f**, **4g**, **4h**, **5b**, **5c**, **5g**), hexane (**6c**), or hexanes−ethyl acetate (**6d**).

***N*-[(3-Nitrophenyl)thio]-4-(ethoxycarbonyl)-2,6-diphenylphenylaminyl (4a):** dark blue fine plates; yield 26%; mp 118−120 °C; IR (KBr) 1705, 1530, 1495, 1345, 1240, 1100, 1055, 1030, 770, 750, 730, 705 cm^{-1}. Anal. Calcd for $C_{27}H_{21}N_2O_4S$: C, 69.06; H, 4.51; N, 5.97. Found: C, 68.77; H, 4.46; N, 5.80.

***N*-[(4-Nitrophenyl)thio]-4-(ethoxycarbonyl)-2,6-diphenylphenylaminyl (4b):** dark greenish black plates; yield 23%; mp 112−114 °C; IR (KBr) 1710, 1570, 1515, 1335, 1240, 1105, 850, 770, 740, 705 cm^{-1}. Anal. Calcd for $C_{27}H_{21}N_2O_4S$: C, 69.06; H, 4.51; N, 5.97. Found: C, 68.83; H, 4.80; N, 5.89.

***N*-[(2,4-Dichlorophenyl)thio]-4-(ethoxycarbonyl)-2,6-diphenylphenylaminyl (4c):** dark blue fine plates; yield 16%; mp 114−116 °C; IR (KBr) 1710, 1565, 1550, 1495, 1445, 1380, 1330, 1240, 1110, 1060, 1035, 820, 779, 710 cm^{-1}. Anal. Calcd for $C_{27}H_{20}Cl_2NO_2S$: C, 65.72; H, 4.09; N, 2.84. Found: C, 65.47; H, 4.15; N, 2.77.

***N*-[(3,5-Dichlorophenyl)thio]-4-(ethoxycarbonyl)-2,6-diphenylphenylaminyl (4d):** dark blue fine prisms; yield 25%; mp 112−114 °C; IR (KBr) 1700, 1555, 1490, 1440, 1410, 1320, 1235, 1105, 1050, 1025, 845, 800, 770, 700, 660 cm^{-1}. Anal. Calcd for $C_{27}H_{20}Cl_2NO_2S$: C, 65.72; H, 4.09; N, 2.84. Found: C, 65.47; H, 4.07; N, 2.75.

***N*-[(3-Nitrophenyl)thio]-4-(ethoxycarbonyl)-2,6-bis(4-chlorophenyl)phenylaminyl (4e):** dark blue fine needles; yield 31%; mp 106−108 °C; IR (KBr) 1705, 1525, 1490, 1345, 1240, 1090, 1045, 1015, 830, 770, 730 cm^{-1}. Anal. Calcd for $C_{27}H_{19}Cl_2N_2O_4S$: C, 60.23; H, 3.56; N, 5.20. Found: C, 60.16; H, 3.61; N, 5.05.

***N*-[(4-Nitrophenyl)thio]-4-(ethoxycarbonyl)-2,6-bis(4-chlorophenyl)phenylaminyl (4f):** dark greenish blue fine needles; yield 18%; mp 128−130 °C; IR (KBr) 1700, 1595, 1570, 1520, 1490, 1340, 1240, 1110, 1090, 1045, 1015, 855, 770, 740 cm^{-1}. Anal. Calcd for $C_{27}H_{19}Cl_2N_2O_4S$: C, 60.23; H, 3.56; N, 5.20. Found: C, 59.99; H, 3.64; N, 5.04.

***N*-[(2,4-Dichlorophenyl)thio]-4-(ethoxycarbonyl)-2,6-bis(4-chlorophenyl)phenylaminyl (4g):** dark blue fine needles; yield 38%; mp 127−128 °C; IR (KBr) 1710, 1490, 1440, 1240, 1110, 1090, 1040, 1015, 820, 770 cm^{-1}. Anal. Calcd for $C_{27}H_{18}Cl_4NO_2S$: C, 57.67; H, 3.23; N, 2.49. Found: C, 57.48; H, 3.19; N, 2.47.

***N*-[(3,5-Dichlorophenyl)thio]-4-(ethoxycarbonyl)-2,6-bis(4-chlorophenyl)phenylaminyl (4h):** dark violet-blue fine needles; yield 36%; mp 116−118 °C; IR (KBr) 1700, 1560, 1490, 1400, 1320, 1240, 1105, 1090, 1040, 1015, 830, 800, 770, 660 cm^{-1}. Anal. Calcd for $C_{27}H_{18}Cl_4NO_2S$: C, 57.67; H, 3.23; N, 2.49. Found: C, 57.53; H, 3.51; N, 2.30.

***N*-[(4-Nitrophenyl)thio]-4-acetyl-2,6-diphenylphenylaminyl (5b):** dark green fine needles; yield 28%; mp 151−152 °C; IR (KBr) 1675, 1595, 1575, 1510, 1420, 1335, 1230, 1105, 1075, 960, 905, 845, 720, 700 cm^{-1}. Anal. Calcd for $C_{26}H_{19}N_2O_3S$: C, 71.04; H, 4.37; N, 6.37. Found: C, 70.85; H, 4.40; N, 6.14.

***N*-[(2,4-Dichlorophenyl)thio]-4-acetyl-2,6-diphenylphenylaminyl (5c):** dark green prisms; yield 52%; mp 102−103 °C; IR (KBr) 1665, 1570, 1490, 1445, 1420, 1380, 1355, 1320, 1230, 1090, 1035, 965, 900, 810, 780, 700, 565 cm^{-1}. Anal. Calcd for $C_{26}H_{18}Cl_2NOS$: C, 67.38; H, 3.92; N, 3.02. Found: C, 67.15; H, 3.96; N, 2.99.

***N*-[(2,4-Dichlorophenyl)thio]-4-acetyl-2,6-bis(4-chlorophenyl)phenylaminyl (5g):** dark green fine needles; yield 22%; mp 133−134 °C; IR (KBr) 1675, 1565, 1490, 1445, 1420, 1230, 1090, 1030, 1015, 965, 840, 820, 740, 720 cm^{-1}. Anal. Calcd for $C_{26}H_{16}Cl_4NOS$: C, 58.66; H, 3.04; N, 2.63. Found: C, 58.40; H, 3.08; N, 2.47.

***N*-[(2,4-Dichlorophenyl)thio]-4-cyano-2,6-diphenylphenylaminyl (6c):** dark blue prisms; yield 23%; mp 104−105 °C; IR (KBr) 2220, 1565, 1550, 1490, 1440, 1415, 1380, 1110, 1090, 1035, 890, 870, 820, 805, 780, 755, 715, 700, 610 cm^{-1}. Anal. Calcd for $C_{25}H_{15}Cl_2N_2S$: C, 67.26; H, 3.39; N, 6.28. Found: C, 66.92; H, 3.25, N, 6.24.

***N*-[(3,5-Dichlorophenyl)thio]-4-cyano-2,6-diphenylphenylaminyl (6d):** dark blue needles; yield 16%; mp 103−104 °C; IR (KBr) 2220, 1560, 1490, 1440, 1420, 1135, 1100, 890, 795, 780, 735, 705, 660, 610 cm^{-1}. Anal. Calcd for $C_{25}H_{15}Cl_2N_2S$: C, 67.26; H, 3.39; N, 6.28. Found: C, 67.07; H, 3.25, N, 6.26.

Product Analysis for Decomposition of 7. Precursor **12** (100 mg, 0.214 mmol) was dissolved in 10 mL of benzene with stirring. After 1.0 g of K_2CO_3 was added, 1.0 g of PbO_2 was added in several portions during 2 min and the resulting mixture was further stirred for 0.5 min. After filtration, the filtrate was evaporated, and the residue was chromatographed on alumina with 1:1 benzene−hexane to give 9.0 mg (0.025 mmol) of 2,4-dichlorophenyl disulfide, 16 mg (0.034 mmol) of unreacted **12**, and 37 mg (0.052 mmol) of **14**. 2,4-Dichlorophenyl disulfide was identified by IR and ^{1}H NMR spectra. The results are shown in Table 3.

***N*-[(2,4-Dichlorophenyl)thio]-*N*′-(4-nitro-2,6-diphenylphenyl)-2,6-diphenyl-1,4-benzoquinone diimine (14):** Red prisms (from hexane); mp 228−230 °C; ^{1}H NMR ($CDCl_3$) δ 6.22−8.28 (m, 27 H); MS *m*/*z* (rel intensity) 707 (M^+, 26), 533 (100), 484 (50), 242 (90). Anal. Calcd for $C_{42}H_{27}Cl_2N_3O_2S$: C, 71.18; H, 3.84; N, 5.93. Found: C, 71.07; H, 4.01; N, 5.76.

Product Analysis for Decomposition of 8. Precursor **13** (200 mg, 0.438 mmol) was dissolved in 20 mL of benzene with stirring. After 2.0 g of K_2CO_3 was added, 2.0 g of PbO_2 was added in several portions during 2 min, and the resulting mixture was further stirred for 0.5 min. After filtration, the filtrate was evaporated, and the residue was chromatographed on alumina with 1:5 benzene−hexane to give 18 mg (0.050 mmol) of 2,4-dichlorophenyl disulfide, 91 mg (0.199 mmol) of unreacted **13**, and 73 mg (0.104 mmol) of **15**. 2,4-Dichlorophenyl disulfide was identified by IR and ^{1}H NMR spectra. The results are shown in Table 3.

***N*-[(2,4-Dichlorophenyl)thio]-*N*′-(4-chloro-2,6-diphenylphenyl)-2,6-diphenyl-1,4-benzoquinone diimine (15):** red prisms (from ethanol); mp 222−224 °C; ^{1}H NMR ($CDCl_3$) δ 6.32−7.46 (m, 27 H); MS *m*/*z* (rel intensity) 698 (M^+, 24), 522 (100), 484 (65), 242 (96). Anal. Calcd for $C_{42}H_{27}Cl_3N_2S$: C, 72.26; H, 3.90; N, 4.01. Found: C, 72.24; H, 3.99; N, 3.97.

X-ray Crystallographic Analysis of 5c.[22,23] A dark green prismatic crystal of $C_{26}H_{18}Cl_2NOS$ (M = 463.40) having approximate dimensions of 0.70 × 0.30 × 0.20 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Cu $K\alpha$ radiation (λ = 1.54178 Å). Monoclinic space group $P2_1/n$, a = 9.0169(9), b = 25.4085(8), c = 10.409(1) Å, β = 108.638(7)°, V = 2259.8(3) Å^3, Z = 4, D_c = 1.362 g cm^{-3}.

The data were collected at a temperature of 23 ± 1 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 110.1°. The linear absorption coefficient, μ, for Cu $K\alpha$ radiation is 35.9 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.66 to 1.00.

The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. Of the 3120 reflections collected, 2443 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 280 variable parameters and converged with unweighted and weighted agreement factors of R = 0.049 and R_w = 0.044.

X-ray Crystallographic Analysis of 6c.[22,23] A dark blue prismatic crystal of $C_{25}H_{15}Cl_2N_2S$ (M = 446.37) having approximate dimensions of 0.40 × 0.20 × 0.70 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Cu $K\alpha$ radiation (λ = 1.54178 Å). Monoclinic space group $P1$, a = 10.939(1), b = 12.186(2), c = 10.029(1) Å, α = 106.03(1), β = 113.255(9), γ = 104.128(10)°, V = 1082.1(3) Å^3, Z = 2, D_c = 1.370 g cm^{-3}.

The data were collected at a temperature of 23 ± 1 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 113.2°. The linear absorption coefficient, μ, for Cu $K\alpha$ radiation is 37.1 cm^{-1}. An empirical absorption correction based on azimuthalscans of several reflections was applied which resulted in transmission factors ranging from 0.55 to 1.00.

(22) The crystallographic computing was done by the TEXSAN structure analysis software.

(23) The authors have deposited atomic coordinates for this structure with the Cambridge Crystallograpic Data Center. The coordinates can be obtained, on request, from the Director, Cambridge Crystallograhic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK.

The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. Of the 2568 reflections collected, 2191 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 331 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.066$ and $R_w = 0.068$.

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Supporting Information Available: X-ray crystallographic data and ORTEP drawings and crystal structures for **5c** and **6c** (29 pages). This material is contained in libraries on microfiche, immediately follows this article in microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.

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