Generation, Isolation, and Characterization of *N*-(Arylthio)-7-*tert*-butyl- and *N*-(Arylthio)-2,7-di-*tert*-butyl-1-pyrenylaminyl Radicals[1]

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N-(Arylthio)-7-*tert*-butyl-1-pyrenylaminyl (**2**) and *N*-[(4-nitrophenyl)thio]-2,7-di-*tert*-butyl-1-pyrenylaminyl radicals (**3**) are prepared by PbO_2 oxidation of *N*-(arylthio)-7-*tert*-butyl-1-aminopyrenes and *N*-[(4-nitrophenyl)thio]-2,7-di-*tert*-butyl-1-aminopyrene, respectively, and studied by ESR and ENDOR spectroscopy. The kinetic ESR study shows that, while aminyls **2** gradually decompose in solution at room temperature, aminyl **3** is quite persistent, even in refluxing benzene, and shows no tendency to dimerize, even at low temperatures. These interesting properties of **3** permit us to isolate **3** as radical crystals in 28–31% yield. The hyperfine splitting (hfs) constants of **2** and **3**, determined by ESR and ENDOR spectroscopic methods, show an extensive delocalization of the unpaired electron onto the pyrene ring. Comparison of the hfs constants of **2** and **3** shows that a more extensive delocalization of the spin into the pyrene ring takes place in **3**. This is accounted for in terms of the difference in the conformations of **2** and **3**.

Introduction

Radical persistence is a function of electronic stabilization and steric protection. Thioaminyls[2] (RṄSR′) are electronically stabilized largely by the conjugative delocalization of the unpaired electron from the nitrogen to the sulfur (–Ṅ–S– ↔ –N̈–Ṡ⁺–). In previous papers, we reported that sterically protected *N*-[(4-nitrophenyl)thio]-2,4,6-tri-*tert*-butylphenylaminyl[3] and *N*-(arylthio)-2,4,6-triphenylphenylaminyl radicals[4] were isolated as pure radical crystals. The recent pursuit of stable free radicals has been stimulated primarily by the suggestion that radical crystals or polyradicals might behave as organic ferromagnets.[5]

As part of a program directed toward the syntheses of high spin or ferromagnetic materials,[6] we have made efforts to search for exceptionally persistent free radicals. Stabilized radicals can be designed by the introduction of a large π-aromatic system to a conjugated π-radical system. In this study, three kinds of pyrene-ring bearing thioaminyl radicals, *N*-(arylthio)-1-pyrenylaminyls **1**, *N*-(arylthio)-7-*tert*-butyl-1-pyrenylaminyls **2**, and *N*-(arylthio)-2,7-di-*tert*-butyl-1-pyrenylaminyls **3** were generated and studied by electron spin resonance (ESR) and electron nuclear double resonance (ENDOR) spectroscopy. It was found that, although aminyls **1** were much less persistent than expected, sterically protected aminyls **2** and **3** were much more persistent. Particularly interesting was **3**, which was exceptionally persistent and isolated as radical crystals. We report herein the generation, ESR and ENDOR spectra, and isolation of these radicals.[7]

Results and Discussion

Generation and ESR Spectra of 2. Aminyls **2** were generated by (1) oxidation of *N*-(arylthio)-7-*tert*-butyl-1-aminopyrenes (**4**) with PbO_2 in benzene and (2) the reaction of **4** with di-*tert*-butyl diperoxyoxalate in benzene. The perester is known to decompose at room temperature in hydrocarbon solvents to give two *tert*-butoxyl radicals.[8] Precursors **4** were obtained by the reaction of 7-*tert*-butyl-1-aminopyrene with unsubstituted and substituted benzenesulfenyl chlorides in the presence of triethylamine (Scheme 1). When PbO_2 was added to a stirred solution of **4** in benzene, the colorless (**4a**), light red (**4c**), or light yellow solution (**4e**) immediately turned wine-red and gave an intense ESR signal due to **2**. However, the wine-red color soon turned dark brownish-red, suggesting that a relatively rapid decomposition of **2** took place. The ESR spectra of **2** were very complex, and the signals were seriously broadened due to the presence of many magnetically unequivalent protons. To simplify the ESR spectra, we deuterated the benzene ring. The deuterated precursors, **4b**, **4d**, and **4f**, were prepared by the above procedure, using the corresponding deuterated benzenesulfenyl chlorides. A typical ESR spectrum is shown in Figure 1. The deuterated aminyls gave a relatively well resolved ESR spectrum, and they were deciphered by

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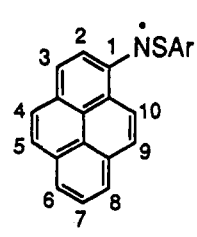
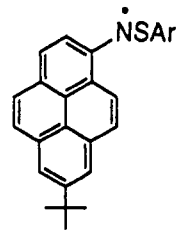
Chart 1



1



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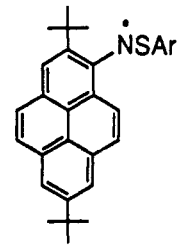


3

a: Ar = Ph

b: Ar = C_6D_5

c: Ar = 4-BrC_6H_4

d: Ar = 4-BrC_6D_4

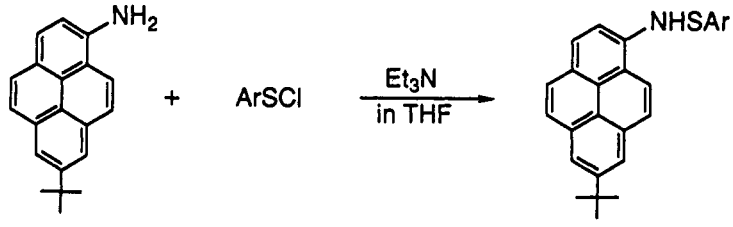
e: Ar = 4-$NO_2C_6H_4$

f: Ar = 4-$NO_2C_6D_4$

a: Ar = 4-$NO_2C_6H_4$

b: Ar = 4-$NO_2C_6D_4$

Scheme 1



4

a: Ar = Ph

b: Ar = C_6D_5

c: Ar = 4-BrC_6H_4

d: Ar = 4-BrC_6D_4

e: Ar = 4-$NO_2C_6H_4$

f: Ar = 4-$NO_2C_6D_4$

computer simulation. The hyperfine splitting (hfs) constants and g values for **2b**, **2d**, and **2f** are summarized in Table 1.

Stabilities of 2. The stabilities of **2** in benzene were measured by following the intensities of their ESR signals at 20 °C. For all **2** radicals, a similar, gradual decomposition was observed and the half-life times ($\tau_{1/2}$) were 6–8 h at 20 °C (the initial radical concentration was $\sim 10^{-4}$ M). The reactivities of **2** toward atmospheric oxygen were examined by measuring the decomposition rates in the presence of atmospheric oxygen, and it was found that aminyls **2** are not destroyed by atmospheric oxygen. Although aminyls **2** are not sufficiently stable to be isolated as radical crystals, they are much more persistent than *N*-(arylthio)phenylaminyl radicals ($\tau_{1/2}$ <20 min in benzene)[9] owing to the electronic stabilization of the unpaired electron by the pyrene ring and steric protection by a *tert*-butyl group at C7.

Generation and ESR Spectra of 3. Aminyls **3** are more highly protected by two *tert*-butyl groups. The corresponding precursors, *N*-(phenylthio)-, *N*-[(4-chlorophenyl)thio]-, and *N*-[(4-bromophenyl)thio]-2,7-di-*tert*-butyl-1-aminopyrenes, were approached by employing the reaction of 2,7-di-*tert*-butyl-1-aminopyrene with the corresponding arenesulfenyl chlorides in the presence of triethylamine (Scheme 2), in a manner similar to **4**. However, the presence of a *tert*-butyl group at C2 prevented the formation of the corresponding **5**. When more reactive 4-nitrobenzenesulfenyl chloride was used, the desired product, *N*-[(4-nitrophenyl)thio]-2,7-di-*tert*-butyl-1-aminopyrene (**5a**), was obtained in 36% yield. Similar steric inhibition of this reaction was previously observed with 2,4,6-tri-*tert*-butylaniline and benzenesulfenyl chlorides.[3] In this case, also, the desired product, *N*-[(4-nitrophenyl)thio]-2,4,6-tri-*tert*-butylaniline, was obtained when 4-nitrobenzenesulfenyl chloride was used.

Generation of **3** was accomplished by oxidation with PbO_2, by the same procedure used for **2**. When PbO_2 was added to a light yellow solution of **5a**, the solution immediately turned dark red and gave an intense ESR signal due to **3a** (Figure 2). The ESR spectrum was simpler than that of **2** because the hydrogen at C2 of the pyrene ring is replaced by a *tert*-butyl group giving rise to no hyperfine splitting. It was difficult, however, to analyze

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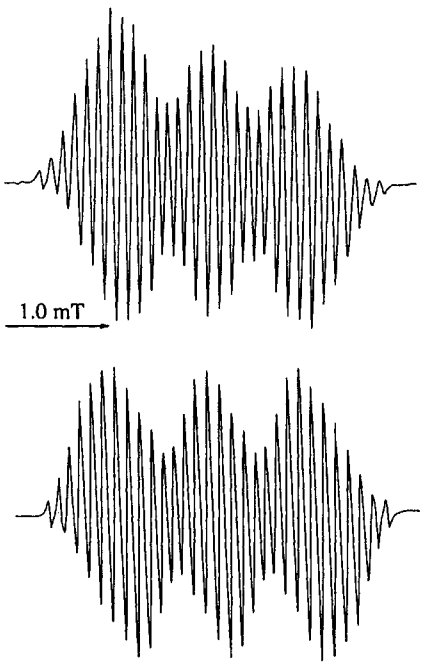
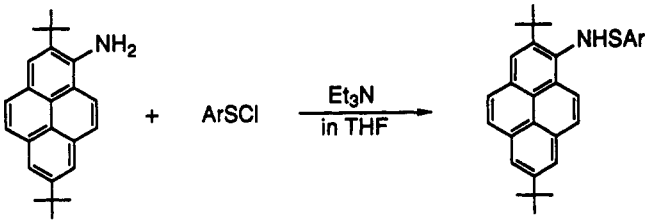


Figure 1. Experimental ESR spectra (top) of **2b** in benzene at 20 °C and a computer-simulated ESR spectrum (bottom) reconstructed by using the hfs constants shown in Table 1 and a line width of 0.0424 mT.

Scheme 2



5

a: Ar = 4-$NO_2C_6H_4$

b: Ar = 4-$NO_2C_6D_4$

the ESR spectrum without the aid of computer simulation. To determine the hfs constants for the benzene ring

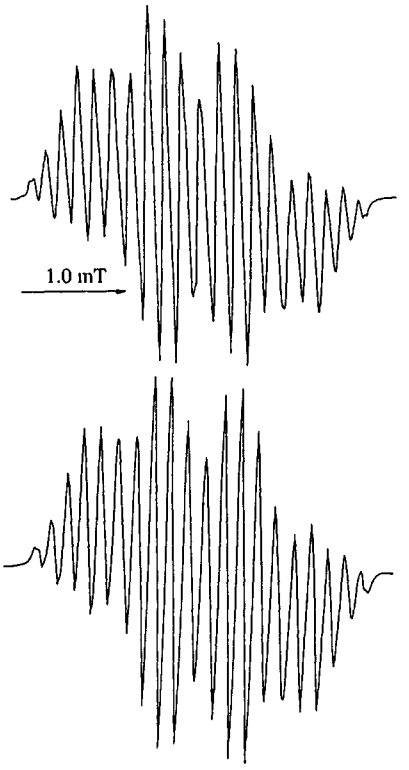
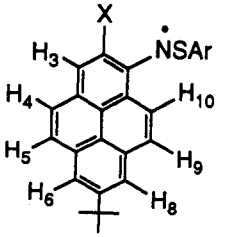


Figure 2. Experimental ESR spectrum (top) of **3a** in benzene at 20 °C and a computer-simulated ESR spectrum (bottom) reconstructed by using the hfs constants shown in Table 1 and a line width of 0.0295 mT.

protons, the corresponding benzene-ring deuterated precursor, *N*-[(4-nitrophenyl-d_4)thio]-2,7-di-*tert*-butyl-1-amionpyrene (**5b**) was prepared from 2,7-di-*tert*-butyl-1-aminopyrene and 4-nitrobenzenesulfenyl-d_4 chloride, and the corresponding aminyl **3b** was generated by oxidation of **5b** with PbO_2. The ESR spectrum of the deuterated aminyl **3b** was very similar to that of **3a**, but the incompletely resolved 1:2:1 triplets, having an interval of 0.041 mT, observed at the outer range of the spectrum of **3a**, were not present. It was thereby confirmed that the triplet hyperfine splitting is due to the ortho protons of the benzene ring. The ESR parameters for **3a** and **3b** determined by the computer simulation method are shown in Table 1.

Table 1. Hyperfine Spitting Constants and *g* Values for 2 and 3[a]



X: H_2 for **2** and *t*-Bu for **3**

radical	Ar	method[b]	a_N[c]	a_H[d] for H_2, H_5, H_6, H_8, H_9	a_H for H_3, H_4, H_{10}	a_{other}	*g*
2b	C_6D_5	ESR[e]	0.874	0.257, 0.231, 0.218, 0.212, 0.203	0.135, 0.110, 0.110		2.0049
2d	4-BrC_6D_4	ESR[e]	0.867	0.254, 0.242, 0.229, 0.216, 0.201	0.134, 0.109, 0.109		2.0050
2f	4-$NO_2C_6D_4$	ESR[e]	0.848	0.270, 0.245, 0.238, 0.230, 0.220	0.147, 0.117, 0.117		2.0046
3a	4-$NO_2C_6H_4$	ESR[e]	0.664	0.363, 0.316, 0.302, 0.298	0.152, 0.150, 0.126	0.041[g]	2.0043
3b	4-$NO_2C_6D_4$	ESR[e]	0.664	0.364, 0.317, 0.302, 0.298	0.151, 0.133, 0.126		2.0043
3b	4-$NO_2C_6D_4$	ENDOR[f]		0.366, 0.321, 0.306, 0.298	0.151, 0.139, 0.121	0.010[h]	

[a] Hyperfine splitting constants are given in mT. [b] The method for determination of hfs constants. [c] The value for the central (–NS–) nitrogen. [d] For **2** the values for H_2, H_5, H_6, H_8, and H_9 are given, and for **3** the values for H_5, H_6, H_8, and H_9 are given. [e] In benzene at 20 °C. The hfs constants are determined by computer simulation. [f] In toluene at –90 °C. [g] The value for the two ortho protons of the benzene ring. [h] The value for the *tert*-butyl protons.

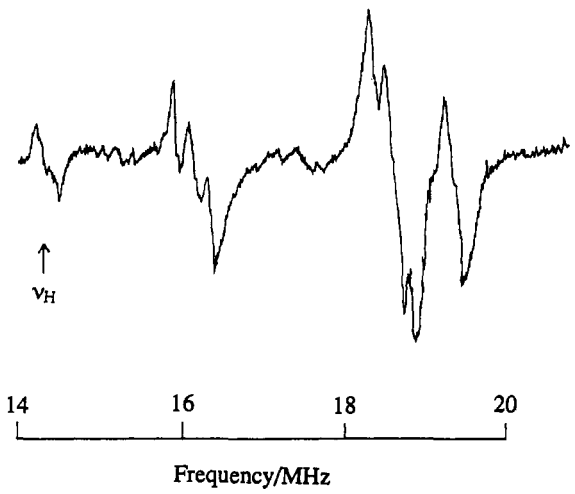


Figure 3. ENDOR spectrum of **3b** in toluene at −90 °C.

ENDOR Spectra of 3b. In order to ascertain the hfs constants by ESR spectroscopy, ENDOR measurements were carried out on the isolated **3b** radical at −90 °C using toluene as a solvent and using a TM_{110} mode cavity as reported previously.[10,11] The results are summarized in Table 1 for comparison.

The ENDOR spectrum of this radical exhibited a good S/N ratio and good resolution, as shown in Figure 3. Seven absorption peaks due to four and three of the two types of protons appear around 19 and 16 MHz regions, respectively, which supports the above-mentioned computer simulation analysis of the ESR spectrum of **3b**. Furthermore, an absorption peak near the free proton frequency (14.3 MHz) was observed, which is likely due to either or both of the *tert*-butyl groups on the pyrene ring. In conclusion, the hfs constants determined for **3** by ESR have been substantiated by the ENDOR measurements.

Stabilities of 3. In contrast to **2**, aminyls **3** were found to be quite persistent. That is, the ESR signal intensity was followed at 20 °C over 1 day, but no or only a small reduction in the ESR signal intensity was observed, regardless of the presence or absence of atmospheric oxygen. Furthermore, the temperature dependence of the ESR signal intensity indicated that the aminyl exhibited no tendency to dimerize in solution, even upon cooling to low temperature, indicating that **3** exists solely as the individual radical. These noteworthy results prompted us to try to isolate **3**.

Isolation of 3. A benzene solution of **5** was stirred in the presence of PbO_2 and K_2CO_3 for 2–3 min. After filtration, the solvent was removed by freeze–drying, and the resulting dark red crystalline powder was crystallized from benzene–hexane to give **3** as reddish black fine needles in 28–31% yield. The structures were confirmed by the IR spectra, which showed no NH absorption, and by satisfactory elemental analyses. The purity of the radical crystals estimated by the solution ESR method using 1,3,5-triphenylverdazyl[12] as the reference was 92–94%. A consistent value (90%) was also obtained from magnetic susceptibility (χ) measurements of the radical crystals with a superconducting quantum interference device (SQUID) magnetometer.[13]

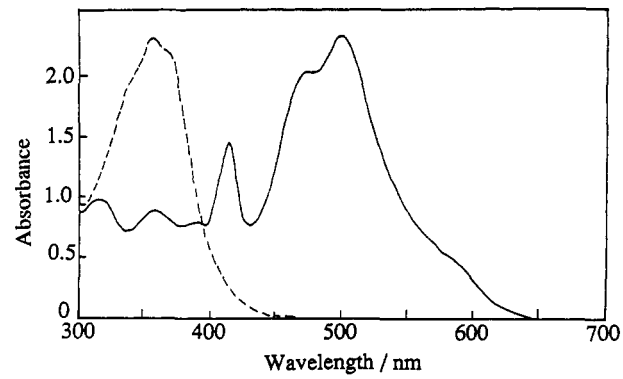


Figure 4. UV–vis spectrum of **3b** (—) and **5a** (- - -) in benzene: **3a**, 8.19×10^{-5} M; **5a**, 9.20×10^{-5} M.

To determine the thermal stability of **3a**, it was heated in refluxing benzene under atmospheric conditions, and the radical concentration was followed by measuring the absorbance at 497 nm, attributable to **3a** (see below). Interestingly, even after 4 h at reflux temperature, no decomposition of **3a** was observed, indicating that **3a** is thermally very stable. Because of this, the crystals of this radical could be stored over a long period of time without decomposition.

The crystal structure of this radical is very interesting, and efforts have been made to obtain radical crystals large enough for X-ray crystallographic analysis. However, all crystallizations, from a variety of solvents, produced only fine needles. Therefore, the X-ray analysis was not feasible.

UV–Vis Spectra of 3. Radicals **3** are characterized by their dark red color. As seen in the UV–vis spectrum of **3a** illustrated in Figure 4, **3a** absorbs at 497 (ϵ 25 500), 471 (22 300), and 412 nm (16 000) in the visible region and at 387 (ϵ 8830), 359 (9910), and 318 nm (10 700) in the UV region. Owing to the strong absorption at 497 nm, aminyl **3a** shows a characteristic red color. When the solvent and reagents used do not have absorptions in the visible region, one can readily determine the radical concentrations by measuring the absorbance at 497 nm.

ESR Parameters. Aminyls **2** have eight magnetically unequivalent protons on the pyrene ring, and aminyls **3** have seven. Although the actual assignment of these protons is almost impossible unless the protons have been regiospecifically deuterated, the protons can be roughly assigned on the basis of the spin density distribution predicted by molecular orbital (MO) calculations. Toward this end, we performed McLachlan–Hückel MO calculations for **1** (Ar = Ph) using the parameters $\alpha_N = \alpha + 0.6\beta$, $\alpha_S = \alpha + \beta$, $\beta_{CN} = 1.1\beta$, $\beta_{NS} = 0.7\beta$, $\beta_{CS} = 0.7\beta$, $\lambda = 0.7$[14] and assuming that the radical is planar. The results of the calculations are shown in Figure 5, from which it is obvious that, among the hydrogen-carrying carbons (C2–C10) of the pyrene ring, the positions of high spin density are C2, C5, C6, C8, and C9, while the positions of low spin density are C3, C4, C7, and C10. On the basis of the MO calculations, the five protons having the larger hfs

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(12) Kuhn, R.; Trischmann, H. *Monatsh. Chem.* **1964**, *95*, 457.
(13) Preliminary SQUID measurements of the **3a** radical crystals performed in the temperature range 1.8–300 K indicated that the interactions among the electron spins were strongly antiferromagnetic.
(14) Miura, Y.; Asada, H.; Kinoshita, M.; Ohta, K. *J. Phys. Chem.* **1983**, *87*, 3450.

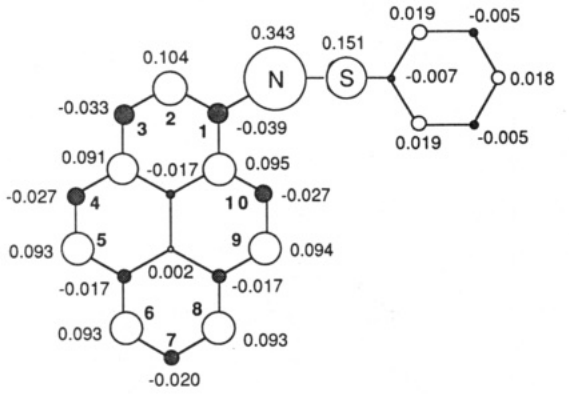

Figure 5. Spin density distribution in **1** (Ar = Ph) predicted by the MacLachlan–Hückel MO calculation; the values refer to the calculated spin density on each atom.

constants are assigned as one of those attached to C2, C5, C6, C8, or C9. The remaining four (for **2**) or three (for **3**) protons, having smaller hfs constants, are assigned as those attached to C3, C4, C7, and C10.

The relatively large hyperfine splitting constants for the pyrene ring protons show that there is an extensive delocalization of the unpaired electron from the nitrogen to the pyrene ring. This leads to a reduction in the spin densities on the (central) nitrogen, sulfur, and the benzene ring. However, the relatively high g values for **2** and **3**, as compared to those (~2.003) of typical nitrogen-centered radicals such as diaryamino and verdazyls radicals,[15] indicate that there is still considerable spin density on the sulfur, which has a large spin-orbit coupling parameter (382 cm^{-1}),[16] which is in accordance with the calculations described above.

Comparison of the hfs constants of **2** and **3** also reveals interesting differences. As found in Table 1, the a_N values for **3** are ~0.20 mT lower than those for **2**. In contrast, the a_H values due to the pyrene ring protons are considerably higher than those for **2**. Furthermore, the g values for **3** are 0.0003–0.0007 lower than those for **2**. These differences in a_N, a_H, and g indicate that delocalization of the unpaired electron from the nitrogen to the pyrene ring is greater in **3** than in **2**.

The most relevant geometric feature of **2** appears to be a *cis* arrangement of the N–S bond and the C1–C2 bond, at C1–N. On the other hand, that of **3** appears to be a *trans* conformation, because of the presence of a *tert*-butyl group at C2. Such a rotation of the –SAr group would not, however, be expected to change the relative amount of the spin densities on the nitrogen and pyrene ring. The most plausible explanation for the differences in a_N, a_H, and g invokes the difference in the planarity (twisting) between the N–SAr π-system and the pyrene π-system. We believe that the conformations of the N–SAr π-systems in **2** and **3** are similar on the basis of a comparison of the a_N and g values of **2** and **3**. If the pyrene ring is more twisted from the N–SAr π-system, the unpaired electron will reside more on the N–SAr π-system, and this leads to increases in a_N and g and decreases in a_H of the pyrene ring protons. The CPK models suggest that the radical molecule of **3** is quite rigid, and hence the corresponding CPK models could not be constructed owing to the large steric crowding around the nitrogen. At present, we cannot present a reliable explanation of why **3** can adopt a more planar (less twisted) conformation, in spite of the large steric crowding around the nitrogen. The steric crowding may force **3** to adopt unusual C1–N–S and/or N–S–C bond angles, leading to a less twisted conformation. Further investigations to clarify this point are in progress.

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Experimental Section

Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were run on a JASCO A-202 spectrophotometer and UV–vis spectra on a Shimadzu UV-2200 spectrophotometer. ^1H NMR spectra were recorded on a JEOL GX-400 spectrometer (400 MHz); chemical shifts (δ) are expressed in parts per million downfield from tetramethylsilane as an internal standard. The terms ph and py refer to benzene ring and pyrene ring protons, respectively. Mass spectra were recorded with a Hitachi M-2000 mass spectrometer. ESR spectra were obtained with a JEOL JES-ME-3X or Bruker ESP 300 spectrometer equipped with an X-band microwave unit and 100-kHz field modulation. Hyperfine splitting constants and g values were determined by the simultaneous measurements with Fremy's salt (a_N = 1.309 mT; g = 2.0057) in K_2CO_3 aqueous solution as a reference.

ENDOR measurements were carried out at –90 °C using toluene as a solvent on a JEOL JES-ME-3X spectrometer. The ENDOR device and its cavity (TM_{110} mode type) were previously described in detail[10] (microwave power 20 mW, radiofrequency power 150 W).

The spin concentrations of **2** and **3** were determined by double integration of the ESR spectra of the sample and reference solutions in benzene. The calibration curve was drawn with the solutions of 1,3,5-triphenylverdazyl[12] using the same ESR cell and solvent and the same instrument settings as for the sample measurements.

The SQUID measurements were performed on a Quantum Design SQUID MPM2 magnetometer in the temperature range 1.8–300 K. The diamagnetic contribution of the sample was estimated from the Pascale diamagnetic constants.

2,7-Di-*tert*-butylpyrene was obtained by the reported method.[17] Benzenesulfenyl,[9,18,19] benzenesulfenyl-d_5,[9] 4-bromobenzenesulfenyl,[18] 4-bromobenzenesulfenyl-d_4,[20] 4-nitrobenzenesulfenyl,[18,19] and 4-nitrobenzenesulfenyl-d_4 chlorides were prepared by bubbling chlorine into a solution of the corresponding benzenethiols or diaryl disulfides in 30–50 mL of CH_2Cl_2 for ca. 20–30 min at 0 °C or room temperature. Benzenesulfenyl and benzenesulfenyl-d_5 chlorides were used after purification by distillation in the following step. The other sulfenyl chlorides were used without purification after the solutions of the sulfenyl chloride in CH_2Cl_2 were concentrated to ca. 5 mL by bubbling nitrogen. Di-*tert*-butyl diperoxyoxalate was prepared by the method of Bartlett *et al.*[8]

***p*-Chloronitrobenzene-d_4.** A mixture of 4.4 mL of concd D_2SO_4 (99.5 atom % D) (98 wt % solution in D_2O) and 6.6 mL of DNO_3 (99 atom % D) (65 wt % solution in D_2O) was added dropwise to 5.0 g (42.5 mmol) of chlorobenzene-d_5 (98.5 atom % D) at 70 °C with stirring. After being stirred at 70 °C for 5 h, the reaction mixture was cooled and poured into a large amount of ice–water. The organic layer was extracted with benzene, and the benzene extract was washed with 5% NaOH and water and dried ($MgSO_4$). After filtration and evaporation, the residue was column chromatographed on silica gel with 1:1 benzene–hexane as an eluant. Crystallization from methanol gave *p*-chloronitrobenzene-d_4 as light yellow needles with mp 85–86 °C in 37% yield (2.52 g, 15.6 mmol).

***p*-Nitrobenzene-d_4-thiol.** This compound was prepared according to the literature procedure for the corresponding

(17) Rodenburg, L.; Brandsma, R.; Tintel, C.; Thuijl, J. van.; Lugtenburg, J.; Cornelisse, J. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 156.
(18) Miura, Y.; Yamamoto, A.; Katsura, Y.; Kinoshita, M. *J. Org. Chem.* **1980**, *45*, 3875.
(19) Kuhle, E. *Synthesis* **1970**, 561.
(20) Miura, Y.; Tanaka, A. *J. Org. Chem.* **1991**, *56*, 3950.

nonlabeled compound.[21] *p*-Chloronitrobenzene-d_4 (2.52 g, 15.6 mmol) was dissolved in 5 mL of ethanol. To this solution were added 0.374 g of sulfur, a solution of 2.8 g of $Na_2S·8H_2O$ in 15 mL of ethanol, and a solution of 0.64 g of NaOH in 40 mL of ethanol. The resulting mixture was refluxed for 2 h and poured into 100 mL of ice–water. After the byproducts (solid) were removed by filtration, the filtrate was acidified with 2 N HCl to give *p*-nitrobenzene-d_4-thiol containing a considerable amount of 4,4′-dinitrophenyl-d_8 disulfide as a light yellow powder in 65% yield (1.61 g, 10.1 mmol). The product was used in the following step without further purification after drying over P_2O_5 in vacuum: MS (70 eV) *m/z* (relative intensity) 316 (4,4′-dinitrodiphenyl disulfide-d_8, 92), 315 (4,4′-dinitrodiphenyl disulfide-d_7, 8).

2-*tert*-Butylpyrene.[22] To a stirred solution of 25.0 g (0.123 mol) of pyrene and 13.8 g (0.149 mol) of 2-chloro-2-methylpropane in 100 mL of CH_2Cl_2 at 0 °C was added 17.6 g of anhydrous $AlCl_3$ in one portion. After the mixture was stirred for 3 h at room temperature, it was poured into a large excess of ice–water. After filtration, the CH_2Cl_2 layer was separated, dried ($MgSO_4$), and evaporated, and the residue was crystallized from methanol to give a 1:9 mixture (22.4 g) of 2,7-di-*tert*-butylpyrene and 2-*tert*-butylpyrene (as determined by a 400-MHz NMR spectrometer). Recrystallization of the mixture from hexane gave pure 2-*tert*-butylpyrene in 63% yield (20.0 g, 0.0775 mol) as yellowish silver plates with mp 110–112 °C. The ^{1}H NMR spectrum completely agreed with the reported values.[16]

7-*tert*-Butyl-1-nitropyrene. This nitro compound was obtained by the procedure of Cornelisse *et al.*[17] with some modifications. Thus, a solution of 12.7 g (49 mmol) of 2-*tert*-butylpyrene in 200 mL of acetic acid was heated to 100–110 °C with stirring. After 3.74 mL of concd HNO_3 (gr. 1.38) was added, the resultant orange solution was stirred at the same temperature for 1 h and poured into a large excess of ice–water. The orange powder collected by filtration was dissolved in CH_2Cl_2, and the solution was washed with a 1 N NaOH solution and then water. After being dried ($MgSO_4$), the solution was evaporated, and the residue was column chromatographed on silica gel with 1:2 benzene–hexane as an eluant. The more mobile light yellow zone gave 2-*tert*-butyl-1-nitropyrene, and the less mobile orange zone gave 7-*tert*-butyl-1-nitropyrene. Crystallization from hexane–benzene gave 2-*tert*-butyl-1-nitropyrene as yellow needles with mp 181–183 °C in 33% yield (4.91 g, 16.2 mmol) and 7-*tert*-butyl-1-nitropyrene as brilliant yellow plates with mp 189–191 °C in 56% yield (8.26 g, 27.2 mmol). The ^{1}H NMR spectra of these compound agreed completely with the reported values.[17]

7-*tert*-Butyl-1-aminopyrene. To a stirred solution of 10 g (33 mmol) of 7-*tert*-butyl-1-nitropyrene in THF (200 mL)–EtOH (100 mL) was added 2.0 g of Pd/C (5%), and hydrogen was bubbled at room temperature. After ca. 5 h, the nitro compound disappeared. After filtration, the solvent was evaporated and the residue was column chromatographed on silica gel with 1:15 ethyl acetate–benzene as an eluant. Crystallization from hexane–benzene gave 7-*tert*-butyl-1-aminopyrene as brilliant yellow plates in 85% yield (7.70 g, 28.2 mmol): mp 152–154 °C; IR (KBr) 3360 (NH_2), 2950 cm^{-1} (*t*-Bu); ^{1}H NMR ($CDCl_3$) δ 1.56 (s, *t*-Bu, 9 H), 3.7 (br s, NH_2, 2 H), 7.37 (d, J = 7.9 Hz, py, 1 H), 7.79 (d, J = 9.2 Hz, py, 1 H), 7.87 (d, J = 9.2 Hz, py, 1 H), 7.94 (d, J = 7.9 Hz, py, 1 H), 7.95 (s, py, 2 H), 8.07 (s, py, 1 H), 8.09 (s, py, 1 H).

The General Procedure for the Preparation of *N*-(Arylthio)-7-*tert*-butyl-1-aminopyrenes (4). To a stirred solution of 1.0 g (3.66 mmol) of 7-*tert*-butyl-1-aminopyrene and 1.0 mL of Et_3N in 80 mL of anhydrous THF was added dropwise 5.49 mmol of arenesulfenyl chloride in 20 mL of anhydrous THF at 0 °C. After being stirred at the same temperature for 2 h, the reaction mixture was filtered and evaporated under reduced pressure, and the residue was column chromatographed on alumina with 1:1 hexane–benzene (**4a–d**) or 1:2 hexane–benzene (**4e** and **4f**) as an eluant.[23] Crystallization from hexane–benzene gave pure crystals of **4a–e**.

(21) Price, C. C.; Stacy, G. W. *J. Am. Chem. Soc.* **1946**, *68*, 498.

(22) Although Cornelisse *et al.* reported that the treatment of pyrene with an excess of 2-chloro-2-methylpropane in CS_2 at 40 °C in the presence of $AlBr_3$ gave pure 2-*tert*-butylpyrene in 99% yield,[17] our following experiment gave a 1:3 mixture of 2,7-di-*tert*-butylpyrene and 2-*tert*-butylpyrene.

***N*-(Phenylthio)-7-*tert*-butyl-1-aminopyrene (4a)**: brilliant yellowish white plates; mp 181–183 °C; yield 25% (0.35 g, 0.917 mmol); IR (KBr) 3370 (NH), 2950 cm^{-1} (*t*-Bu); ^{1}H NMR ($CDCl_3$) δ 1.57 (s, *t*-Bu, 9 H), 6.20 (s, NH, 1 H), 7.10–7.25 (m, ph, 5H), 7.84 (d, J = 9.2 Hz, py, 1 H), 7.89 (d, J = 9.2 Hz, py, 1 H), 7.98 (d, J = 9 Hz, py, 1 H), 8.00 (d, J = 9 Hz, py, 1 H), 8.02 (d, J = 9 Hz, py, 1 H), 8.04 (d, J = 9 Hz, py, 1 H), 8.124 (s, py, 1 H), 8.128 (s, py, 1 H). Anal. Calcd for $C_{26}H_{23}NS$: C, 81.85; H, 6.08; N, 3.67. Found: C, 82.05; H, 6.16; N, 3.59.

***N*-(Phenylthio-d_5)-7-*tert*-butyl-1-aminopyrene (4b)**: brilliant yellowish white plate; yield 30% (0.42 g, 1.09 mmol); mp 176–178 °C; IR (KBr) 3370 (NH), 2950 cm^{-1} (*t*-Bu); ^{1}H NMR ($CDCl_3$) δ 1.57 (s, *t*-Bu, 9 H), 6.21 (s, NH, 1 H), 7.84 (d, J = 9.2 Hz, py, 1 H), 7.90 (d, J = 9.2 Hz, py, 1 H), 7.98 (d, J = 9 Hz, py, 1 H), 8.00 (d, J = 9 Hz, py, 1 H), 8.02 (d, J = 9 Hz, py, 1 H), 8.04 (d, J = 9 Hz, py, 1 H), 8.13 (s, py, 2 H). Anal. Calcd for $C_{26}H_{18}D_5NS$: C, 80.79; H, 6.00; N, 3.62. Found: C, 80.62; H, 6.10; N, 3.43.

***N*-[(4-Bromophenyl)thio]-7-*tert*-butyl-1-aminopyrene (4c)**: light red plates; yield 23% (0.38 g, 0.83 mmol); mp 152–154 °C; IR (KBr) 3370 (NH), 2950 cm^{-1} (*t*-Bu); ^{1}H NMR ($CDCl_3$) δ 1.57 (s, *t*-Bu, 9 H), 6.14 (s, NH, 1 H), 7.11 (d, J = 8.9 Hz, ph 2 H), 7.34 (d, J = 8.9 Hz, ph 2 H), 7.85 (d, J = 9.2 Hz, py, 1 H), 7.89 (d, J = 9.2 Hz, py, 1 H), 7.91 (d, J = 8.5 Hz, py, 1 H), 7.98 (d, J = 9.2 Hz, py, 1 H), 8.01 (d, J = 8.5 Hz, py, 1 H), 8.03 (d, J = 9.2 Hz, py, 1 H), 8.13 (s, py, 1 H), 8.14 (s, py, 1 H). Anal. Calcd for $C_{26}H_{22}BrNS$: C, 67.82; H, 4.82; N, 3.04. Found: C, 68.08; H, 4.94; N, 3.17.

***N*-[(4-Bromophenyl-d_4)-7-*tert*-butyl-1-aminopyrene (4d)**: light red plates; yield 15% (0.26 g, 0.56 mmol); mp 150–152 °C; IR (KBr) 3370 (NH), 2950 cm^{-1} (*t*-Bu); ^{1}H NMR ($CDCl_3$) δ 1.57 (s, *t*-Bu, 9 H), 6.12 (s, NH, 1 H), 7.84 (d, J = 9.2 Hz, py, 1 H), 7.89 (d, J = 9.2 Hz, py, 1 H), 7.91 (d, J = 8.5 Hz, py, 1 H), 7.96 (d, J = 9.2 Hz, py, 1 H), 8.00 (d, J = 8.5 Hz, py, 1 H), 8.02 (d, J = 9.2 Hz, py, 1 H), 8.13 (s, py, 1 H), 8.14 (s, py, 1 H). Anal. Calcd for $C_{26}H_{18}BrD_4NS$: C, 67.24; H, 4.78; N, 3.02. Found: C, 67.41; H, 4.93; N, 2.96.

***N*-[(4-Nitrophenyl)thio]-7-*tert*-butyl-1-aminopyrene (4e)**: orange fine needles; mp 185–187 °C; yield 36% (0.558 g, 1.31 mmol); IR (KBr) 3370 (NH), 2950 cm^{-1} (*t*-Bu); ^{1}H NMR ($CDCl_3$) δ 1.58 (s, *t*-Bu, 9 H), 6.20 (s, NH, 1 H), 7.38 (d, J = 9.2 Hz, ph, 2 H), 7.86 (d, J = 8.5 Hz, py, 1 H), 7.89 (d, J = 9.2 Hz, py, 1 H), 7.92 (d, J = 9.2 Hz, py, 1 H), 8.03 (d, J = 8.5 Hz, py, 1 H), 8.04 (d, J = 9.2 Hz, py, 1 H), 8.11 (d, J = 9.2 Hz, py, 1 H), 8.12 (d, J = 9.2 Hz, ph, 2 H), 8.17 (s, py, 2 H). Anal. Calcd for $C_{26}H_{22}N_2O_2S$: C, 73.21; H, 5.20; N, 6.57. Found: C, 73.58; H, 5.42; N, 6.25.

***N*-[(4-Nitrophenyl-d_4)thio]-7-*tert*-butyl-1-aminopyrene (4f)**: orange fine needles; mp 185–187 °C; yield 49% (0.768 g, 1.78 mmol); IR (KBr) 3370 (NH), 2950 cm^{-1} (*t*-Bu); ^{1}H NMR ($CDCl_3$) δ 1.58 (s, *t*-Bu, 9 H), 6.19 (s, NH, 1 H), 7.84 (d, J = 8.5 Hz, py, 1 H), 7.89 (d, J = 9.2 Hz, py, 1 H), 7.91 (d, J = 9.2 Hz, py, 1 H), 8.03 (d, J = 8.5 Hz, py, 1 H), 8.04 (d, J = 9.2 Hz, py, 1 H), 8.11 (d, J = 9.2 Hz, py, 1 H), 8.17 (s, py, 2 H). Anal. Calcd for $C_{26}H_{18}D_4N_2O_2S$: C, 72.53; H, 5.15; N, 6.51. Found: C, 72.71; H, 5.30; N, 6.19.

2,7-Di-*tert*-butyl-1-nitropyrene. The nitro compound was obtained according to the procedure of Cornelisse *et al.*[17] with some modifications. Thus, a mixture of 10.0 g (31.8 mmol) of 2,7-di-*tert*-butylpyrene in 500 mL of acetic acid was stirred and heated to 110–115 °C with stirring to become homogeneous. To this solution was added 2.34 mL of concd HNO_3 (d 1.38) in one portion, and the resultant solution was stirred at 110–115 °C for 1 h. After cooling, the solution was poured into a large excess of ice–water, and the crystals deposited were collected by filtration. After being washed with water, the crystals were dissolved in 200 mL of CH_2Cl_2, and the CH_2Cl_2 solution was washed with 5% NaOH and water and dried ($MgSO_4$). After filtration and evaporation, the residue was column chromatographed on silica gel (Wako gel C-200) with 1:5 benzene–hexane as an eluant. Crystallization from hexane–benzene gave 2,7-di-*tert*-butyl-1-nitropyrene as light yellow prisms in 82% yield (9.40

(23) During the column chromatography, part of the product may be decomposed to give 7-*tert*-butyl-1-aminopyrene or 2,7-di-*tert*-butyl-1-aminopyrene and diaryl disulfide.

g, 26.1 mmol): mp 174–175 °C. The ^{1}H NMR spectrum agreed completely with the reported values.

2,7-Di-*tert*-butyl-1-aminopyrene. Onto sodium amalgam, prepared from 21.4 g of sodium and 500 g of mercury, were placed 8.76 g (24.4 mmol) of 2,7-di-*tert*-butyl-1-nitropyrene and 357 mL of anhydrous methanol. After the mixture was gently refluxed over the sodium amalgam for 12 h, the hot methanol solution was poured into a large excess of water to give powdery crystals. The remaining crystals on the sodium amalgam were dissolved in hot methanol, and the solution was poured into a large excess of ice–water. The crystals deposited were collected by filtration, washed with water, dried, and column chromatographed on silica gel with 1:1 benzene–hexane. Crystallization from hexane–benzene gave light yellow prisms in 50% yields (4.00 g, 12.1 mmol): mp 263–265 °C; ^{1}H NMR ($CDCl_3$) δ 1.55 (s, *t*-Bu, 9H), 1.66 (s, *t*-Bu, 9H), ca. 4.2 (br s, NH_2, 2H), 7.87–8.06 (m, py, 7 H).

***N*-[(4-Nitrophenyl)thio]-2,7-di-*tert*-butyl-1-aminopyrene (5a).** To a stirred solution of 1.00 g (3.04 mmol) of 2,7-di-*tert*-butyl-1-aminopyrene and 0.8 mL of Et_3N in 50 mL of anhydrous THF was added dropwise at 0 °C a solution of 4-nitrobenzenesulfenyl chloride, prepared from 0.70 g (2.27 mmol) of 4,4′-dinitrodiphenyl disulfide, in 10 mL of anhydrous THF. After being stirred for 2 h at 0 °C, the reaction mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was column chromatographed on alumina using 1:2 hexane–benzene as an eluant.[23] Crystallization from hexane–benzene gave **5a** as yellow fine needles in 40% yield (0.579 g, 1.20 mmol): mp 179–180 °C; IR (KBr) 3330 (NH), 2920 (*t*-Bu) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.54 (s, *t*-Bu, 9H), 1.75 (s, *t*-Bu, 9 H), 5.94 (s, NH, 1 H), 7.77 (d, J = 9.2 Hz, ph, 2H), 7.81 (d, J = 9.5 Hz, py, 1 H), 7.96 (s, py, 2 H), 8.01 (d, J = 9.5 Hz, py, 1 H), 8.09 (s, py, 1 H), 8.15 (s, py, 2 H), 8.34 (d, J = 8.9 Hz, ph, 2 H). Anal. Calcd for $C_{30}H_{30}N_2O_2S$: C, 74.66; H, 6.27; N, 5.81. Found: C, 74.51; H, 6.29; N, 5.64.

***N*-[(4-Nitrophenyl)thio]-2,7-di-*tert*-butyl-1-pyrenylaminyl Radical (3a).** **5a** (0.100 g, 0.207 mmol) was dissolved in 20 mL of benzene by stirring. After 0.90 g of K_2CO_3 was added, 0.90 g of PbO_2 was added in a few portions during 2 min, and stirring was continued for an additional 0.5 min. After filtration, the benzene was removed by freeze–drying, the residual red crystalline powder was dissolved in a minimum amount of benzene, and hexane was added. On cooling, **3a** was obtained as reddish black fine needles in 31% yield (31 mg, 0.064 mmol): mp 190–192 °C; IR (KBr) 2930, 1565, 1510, 1465, 1330, 1220, 1160, 1100, 1070, 850, 810, 730 cm^{-1}; UV–vis (benzene) 497 (ϵ 25 500), 471 (sh, 22 300), 412 (16 000), 387 (8830), 359 (9910), 318 nm (10 700). Anal. Calcd for $C_{30}H_{29}N_2O_2S$: C, 74.81; H, 6.07; N, 5.82. Found: C, 74.98; H, 6.07; N, 5.76.

***N*-[(4-Nitrophenyl-d_4)thio]-2,7-di-*tert*-butyl-1-aminopyrene (5b).** By the same procedure as for **5a**, 1.00 g (3.04 mmol) of 2,7-di-*tert*-butyl-1-aminopyrene was allowed to react with 4-nitrobenzenesulfenyl-d_4 chloride, prepared from 0.72 g (4.54 mmol) of 4-nitrobenzene-d_4-thiol, in the presence of 0.8 mL of Et_3N at 0 °C. After filtration and evaporation, the residue was column chromatographed on alumina using 1:2 hexane–benzene as an eluant.[23] Crystallization from benzene–hexane gave **5b** as yellow fine needles in 35% yield (0.524 g, 1.07 mmol): mp 183–185 °C; IR (KBr) 3320 (NH) and 2920 cm^{-1} (*t*-Bu); ^{1}H NMR ($CDCl_3$) δ 1.54 (s, *t*-Bu, 9 H), 1.74 (s, *t*-Bu, 9 H), 5.93 (s, NH, 1 H), 7.81 (d, J = 9.5 Hz, py, 1 H), 7.95 (s, py, 2 H), 8.01 (d, J = 9.5 Hz, py, 1 H), 8.09 (s, py, 1 H), 8.14 (s, py, 2 H). Anal. Calcd for $C_{30}H_{28}D_4N_2O_2S$: C, 74.04; H, 6.21; N, 5.76. Found: C, 73.76; H, 6.23; N, 5.65.

***N*-[(4-Nitrophenyl-d_4)thio]-2,7-di-*tert*-butyl-1-pyrenylaminyl Radical (3b).** By the same procedure as for **3a**, 0.100 g (0.205 mmol) of **5b** was treated with 0.90 g of PbO_2 and 0.9 g of K_2CO_3 in benzene. After removal of the solvent by freeze–drying, the red crystalline residue was dissolved in a minimum amount of benzene and hexane was added. On cooling, **3b** was given as reddish black fine needles in 28% yield (28 mg, 0.058 mmol): mp 195–197 °C; IR (KBr) 2950, 1570, 1545, 1510, 1475, 1355, 1330, 1225, 1170, 1090, 1040, 915, 900, 885, 870, 860, 850, 820, 810, 735, 715, 685, 660, 600 cm^{-1}. Anal. Calcd for $C_{30}H_{25}D_4H_2O_2S$: C, 74.19; H, 6.02; N, 5.77. Found: C, 74.57; H, 6.23; N, 5.55.

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