

**ESR and  $^1\text{H}$  ENDOR Spectra of Partly Deuterated  $N$ -[(4-Nitrophenyl)thio]-2,7-di-*tert*-butyl-1-pyrenylaminyl Radical. Assignments of the Pyrene Ring Protons<sup>1</sup>**

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In a previous paper we reported the generation and isolation and ESR and  $^1\text{H}$  ENDOR spectra of  $N$ -[(4-nitrophenyl)thio]-2,7-di-*tert*-butyl-1-pyrenylaminyl (1) and  $N$ -[(4-nitrophenyl- $d_4$ )thio]-2,7-di-*tert*-butyl-1-pyrenylaminyl (2).<sup>2</sup> These radicals are quite persistent even in the presence of oxygen and can be isolated as radical crystals. As can be seen from their structures, they have seven magnetically nonequivalent protons in the pyrene ring. Their hyperfine coupling (hfc) constants were unequivocally determined by the ESR and ENDOR measurements, but reliable assignments of the hfc constants were impossible because partial deuteration of the pyrene ring was not carried out. Since 2,7-di-*tert*-butylpyrene can be prepared from toluene in nine steps,<sup>3</sup> 2,7-di-*tert*-butylpyrene-1,3,6,8- $d_4$  may be obtained from toluene-2,3,4,5,6- $d_5$  by following the synthetic procedure reported for the nonlabeled 2,7-di-*tert*-butylpyrene. However, this procedure is very tedious and not economical. In the course of our recent study of preparation of deuterated compounds, we have found a convenient procedure for deuteration of the pyrene ring.<sup>4</sup> Thus, when 2,7-di-*tert*-butyl-4,5,9,10-tetrabromopyrene (5) was treated in refluxing  $\text{CH}_3\text{OD}$  for a few hours over 4.2 wt % sodium amalgam, 2,7-di-*tert*-butylpyrene-4,5,9,10- $d_4$  (6) with a high isotopic purity (89%) was obtained in good yield. By using this partly deuterated pyrene, we could prepare  $N$ -[(4-nitrophenyl)thio]-2,7-di-*tert*-butyl-1-pyrenylaminyl-4,5,9,10- $d_4$  radical (3). Herein we report a convenient deuteration of the pyrene ring, ESR and ENDOR spectra of 3, and reliable assignments of the pyrene ring protons.

Reductive deuteration of 5 was carried out by treating a solution of 5 in refluxing  $\text{CH}_3\text{OD}$ –benzene for 4 h over 4.2 wt % sodium amalgam. After column chromatographic separation, the deuterated 6 compound with an isotopic purity of 89% was obtained in 69% yield. Since 5 was poorly soluble in methanol, even at the reflux temperature, benzene was added to dissolve 5 completely in the solvent. The isotopic purity of 6 was determined by  $^1\text{H}$  NMR spectroscopy. Since the undeuterated protons at  $\text{C}_4$ ,  $\text{C}_5$ ,  $\text{C}_9$ , and  $\text{C}_{10}$  had an absorption peak at 8.02 ppm, while the protons at  $\text{C}_1$ ,  $\text{C}_3$ ,  $\text{C}_6$ , and  $\text{C}_8$  had an absorption peak at 8.18 ppm, the isotopic purity was determined by the ratio of the intensity of the peak at 8.02 ppm to that at 8.18 ppm. Also, the mass spectral data gave the following: 6- $d_4$ , 57; 6- $d_3$ , 32; 6- $d_2$ , 9.4; 6- $d_1$ , 1.3% (87% isotope purity).

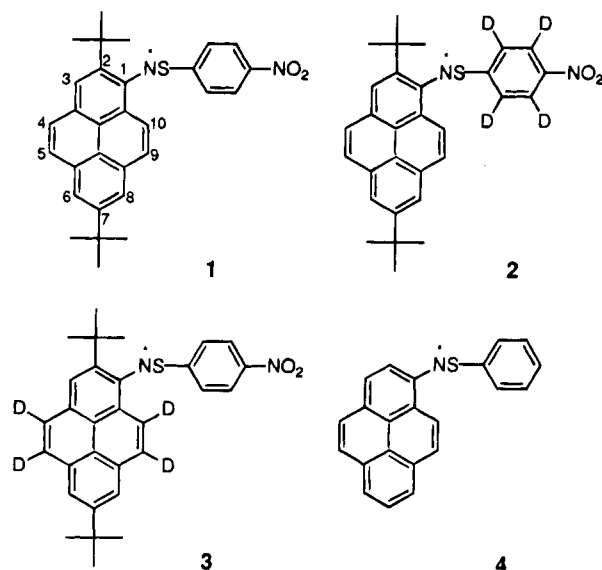
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Chart 1



The preparation of  $N$ -[(4-nitrophenyl)thio]-2,7-di-*tert*-butyl-1-aminopyrene-4,5,9,10- $d_4$  is shown in Scheme 1. Nitration of 6 was carried out by treating it with  $\text{HNO}_3$  in acetic acid. The nitropyrene was then reduced in anhydrous methanol over 4.4% sodium amalgam. The isotope purity of the aminopyrene determined by mass spectroscopy was 87%, indicating that no reduction in the isotope purity took place during the nitration and reduction. Aminyl 3 was generated by  $\text{PbO}_2$  oxidation of 7 in benzene, and its isolation was accomplished by the same procedure as for 1 and 2.<sup>2</sup>

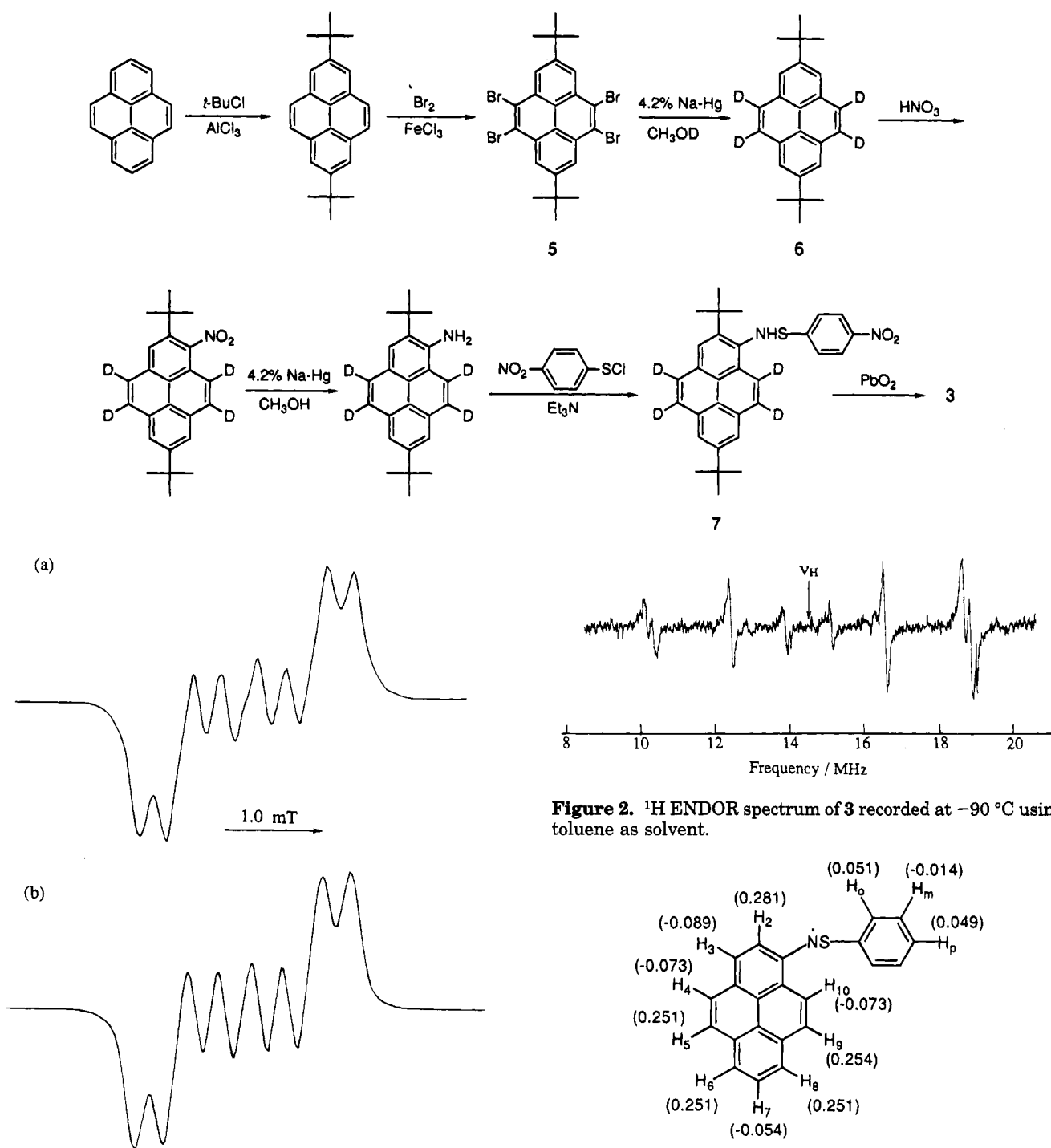
The ESR spectrum of 3 was measured at 20 °C in benzene. As found in Figure 1, the ESR spectrum was very broad because of the unresolved hyperfine couplings due to some protons in the pyrene and benzene rings and some deuteriums in the pyrene ring. We therefore measured the  $^1\text{H}$  ENDOR spectrum of 3 at –90 °C in toluene. As shown by Figure 2, a high resolution ENDOR spectrum with a good S/N ratio was obtained after 200 accumulations with a low frequency modulation depth (50 kHz). In the figure, four pairs of signals are observed, from which four kinds of hfc constants (0.308, 0.294, 0.149, and 0.044 mT) were determined.

Among the four hfc constants, the smallest one (0.044 mT) was unequivocally due to the ortho protons of the benzene ring because disappearance of this coupling was observed in the ESR spectrum of the benzene ring-deuterated aminyl 2.<sup>2</sup> On the other hand, the hfc constant of 0.149 mT was assigned to  $\text{H}_3$ , and the remaining two hfc constants (0.308 and 0.294 mT) were assigned to  $\text{H}_5$  and  $\text{H}_8$  on the basis of the McLachlan MO calculations of 4 (see Figure 3),<sup>5</sup> which predict a high spin density on  $\text{C}_5$ ,  $\text{C}_6$ ,  $\text{C}_8$ , and  $\text{C}_9$ . By using the following hfc constants: 0.664 (1N), 0.308 (1H), 0.294 (1H), 0.149 (1H), 0.148 (1H), 0.044 (2H), 0.056 [1D,  $0.154 \times a(\text{H}_5$  or  $\text{H}_9)$ ], and 0.049 mT [1D,  $0.154 \times a(\text{H}_9$  or  $\text{H}_5)$ ] ( $0.153 = a_{\text{D}}/a_{\text{H}}$ ), the experimental ESR spectrum was satisfactorily reconstructed by computer simulation, as shown in Figure 1.

Comparison of the hfc constants between 1 and 3 allowed the assignments of  $\text{H}_4$ ,  $\text{H}_5$ ,  $\text{H}_9$ , and  $\text{H}_{10}$  to be made. The MO calculations predict that the spin densi-

(5) For the McLachlan MO calculations, see ref 2.

Scheme 1



**Figure 1.** Experimental (a) and computer-simulated ESR spectra (b) of **3**. The experimental spectrum was obtained at  $20^\circ\text{C}$  using benzene as solvent, and the computer-simulated spectrum was reconstructed using the hfc constants shown in Table 1 and 0.056 (1D) and 0.049 mT (1D), and a peak-to-peak line width of 0.090 mT.

ties on  $\text{C}_5$  and  $\text{C}_9$  are much higher than those on  $\text{C}_4$  and  $\text{C}_{10}$ . We, therefore, assign the hfc constants of 0.363 and 0.316 mT (for **1**) to  $\text{H}_5$  and  $\text{H}_9$ , and the hfc constants of 0.150 and 0.126 mT to  $\text{H}_4$  and  $\text{H}_{10}$ . In Table 1 the summary of the assignments of the proton hfc constants for **1–3** is described.

In the above assignments of the proton hfc constants, distinction between the pairs of  $\text{H}_4$  and  $\text{H}_{10}$ ,  $\text{H}_5$  and  $\text{H}_9$ , and  $\text{H}_6$  and  $\text{H}_8$  was not made. As seen from Table 1,

**Figure 2.**  $^1\text{H}$  ENDOR spectrum of **3** recorded at  $-90^\circ\text{C}$  using toluene as solvent.

**Figure 3.** Proton hyperfine coupling constants predicted by the McLachlan MO calculations using the McConnell equation ( $a_x = Q_x Q_x$ , where  $Q_x$  is  $-2.7$  mT).

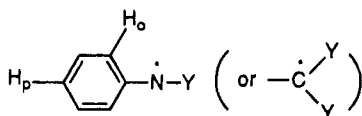
there is a considerable difference in the hfc constants between  $\text{H}_4$  and  $\text{H}_{10}$  ( $1.24 = 0.150$  mT/0.126 mT) and between  $\text{H}_5$  and  $\text{H}_9$  ( $1.15 = 0.363$  mT/0.316 mT). The  $\text{C}_4$  and  $\text{C}_5$  positions are para to the radical center, while the  $\text{C}_9$  and  $\text{C}_{10}$  positions are ortho to the radical center. In general, the hfc constants for the para protons are 1.1–1.2 times larger than those for the corresponding ortho protons in the radicals of the type of **8**, where the unpaired electron is accommodated in the singly occupied  $\pi$ -conjugated system. For example, when Y in  $-\text{NY}$  is Ph,<sup>6</sup> OPh,<sup>7</sup> and SPh,<sup>8</sup> the ratios of  $a(\text{H}_p)/a(\text{H}_o)$  are 1.16, 1.08, and 1.13, respectively. According to this rule, we can

Table 1. Hyperfine Coupling Constants of 3 and Comparison of Them with Those for 1 and 2<sup>a</sup>

| radical | method <sup>b</sup> | $\alpha_N^c$ | $\alpha_{H-5}$ and $-9$ | $\alpha_{H-6}$ and $-8$ | $\alpha_{H-3}$ | $\alpha_{H-4}$ and $-10$ | $\alpha_{\text{other}}$ | $g$    |
|---------|---------------------|--------------|-------------------------|-------------------------|----------------|--------------------------|-------------------------|--------|
| 1       | ESR <sup>d</sup>    | 0.664        | 0.363, 0.316            | 0.302, 0.298            | 0.152          | 0.150, 0.126             | 0.041 <sup>e</sup>      | 2.0043 |
| 2       | ESR <sup>d</sup>    | 0.664        | 0.364, 0.317            | 0.302, 0.298            | 0.151          | 0.133, 0.126             |                         | 2.0043 |
| 2       | ENDOR <sup>f</sup>  |              | 0.366, 0.321            | 0.306, 0.298            | 0.151          | 0.139, 0.121             | 0.010 <sup>g</sup>      |        |
| 3       | ESR <sup>d</sup>    | 0.664        |                         | 0.308, 0.294            | 0.149          |                          | 0.044 <sup>e</sup>      | 2.0043 |
| 3       | ENDOR <sup>f</sup>  |              |                         | 0.308, 0.294            | 0.149          |                          | 0.044 <sup>e</sup>      |        |

<sup>a</sup> Hyperfine coupling (hfc) constants are given in mT. <sup>b</sup> The method for determination of the hfc constants. <sup>c</sup> The value for the central nitrogen. <sup>d</sup> In benzene at 20 °C. The hfc constants are determined by computer simulation of the experimental ESR spectrum. <sup>e</sup> The value for the ortho protons of the benzene ring. <sup>f</sup> In toluene at -90 °C. <sup>g</sup> The value for the *tert*-butyl protons.

Chart 2



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tentatively assign the hfc constant of 0.363 mT to H<sub>5</sub>, and the hfc constant of 0.316 mT to H<sub>9</sub>. Similarly, the hfc constant of 0.150 mT is assigned to H<sub>4</sub>, and the hfc constant of 0.126 mT to H<sub>10</sub>. In the case of H<sub>6</sub> and H<sub>8</sub>, on the other hand, the difference in the hfc constants is smaller (1.02 = 0.302 mT/0.298 mT) because H<sub>6</sub> and H<sub>8</sub> are farther from the radical center than are H<sub>4</sub> and H<sub>10</sub> and H<sub>5</sub> and H<sub>9</sub>. If H<sub>6</sub> and H<sub>8</sub> are boldly assigned in a similar manner, the hfc constant of 0.302 mT is assigned to H<sub>8</sub>, and the hfc constant of 0.298 mT to H<sub>6</sub>.

In summary, the proton hfc constants for the pyrene ring-bearing thioaminyl 1, were assigned by measuring the ESR and ENDOR spectra of a partly deuterated thioaminyl radical 3. A novel procedure for the preparation of deuterated compounds from the corresponding bromo compounds by reductive debromination is found. Since this procedure is convenient and economical and expected to give isotopic high purities, it may be useful for the syntheses of deuterated compounds. Further investigations on the deuteration of bromo compounds by this procedure are in progress. The results will be published elsewhere.

## Experimental Section

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were obtained on a JASCO A-202 spectrophotometer. <sup>1</sup>H NMR spectra were recorded with a JEOL  $\alpha$ -400 spectrometer (400 MHz); chemical shifts ( $\delta$ ) are expressed in parts per million downfield from tetramethylsilane as internal standard. Mass spectra were recorded with a JEOL D-300 spectrometer at 70 eV by direct insertion.

ESR spectra were measured on a JEOL JES-ME-3X spectrometer equipped with an X-band microwave unit and 100 kHz field modulation. The hfc constants and  $g$  value were determined by the simultaneous measurements with Fremy's salt in a K<sub>2</sub>CO<sub>3</sub> aqueous solution ( $\alpha_N = 1.309$  mT,  $g = 2.0057$ ) as reference.

ENDOR measurements were carried out at -90 °C on a Bruker (300/350) ENDOR spectrometer equipped with a TM<sub>011</sub> mode microwave cavity operating at X-band using toluene as solvent.

2,7-Di-*tert*-butylpyrene<sup>9</sup> and 4-nitrobenzenesulfonyl chloride<sup>10,11</sup> were obtained by the reported methods. Methanol-*d*<sub>1</sub> (99.5 atom % D) (purchased from Aldrich) was used without any further purification. Anhydrous methanol was obtained by

distillation from Mg(OMe)<sub>2</sub>. Dry benzene and dry THF were obtained by distillation from sodium and sodium-benzophenone, respectively.

**2,7-*tert*-Butyl-4,5,9,10-tetrabromopyrene (5).** To a stirred mixture of 4.00 g (12.7 mmol) of 2,7-di-*tert*-butylpyrene and 4.0 g of Fe powder in 200 mL of CCl<sub>4</sub> was added dropwise a solution of 12.4 g (78 mmol) of bromine in 40 mL of CCl<sub>4</sub> at room temperature. After completion of the addition, the resulting mixture was stirred for 4 h and poured into a large excess of ice-water. The organic layer was separated, washed with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and then water, and dried (MgSO<sub>4</sub>). After evaporation, the residue was crystallized from hexane-benzene to give 5 as colorless needles with mp 289–291 °C (lit.<sup>12</sup> 287–288 °C) in 80% yield (6.43 g, 10.2 mmol): <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.62 (s, *t*-Bu, 18 H), 8.86 (s, py, 4H).

**2,7-Di-*tert*-butylpyrene-4,5,9,10-*d*<sub>4</sub> (6).** A solution of 1.00 g (1.59 mmol) of 5 in 10 mL of CH<sub>3</sub>OD and 20 mL of dry benzene was refluxed over 33 g of 4.2 wt % of sodium amalgam under dry nitrogen. After 4 h, the organic layer was poured into a large excess of ice-water, separated, dried (MgSO<sub>4</sub>), and evaporated, and the residue was chromatographed on silica gel (Wako gel, C200) with hexane as eluant to give 6 in 69% yield (0.35 g, 1.10 mmol): mp 209–211 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.58 (s, *t*-Bu, 18 H), 8.18 (s, 4H). The isotropic purity (89%) was determined by the ratio of the intensity of the peak at 8.02 ppm due to the undeuterated H<sub>4</sub>, H<sub>5</sub>, H<sub>9</sub>, and H<sub>10</sub> to that at 8.18 ppm due to the magnetically equivalent H<sub>1</sub>, H<sub>3</sub>, H<sub>6</sub>, and H<sub>8</sub>: MS (70 eV)  $m/z$  (relative intensity) 320 (5), 319 (27), 318 (M<sup>+</sup>, 100), 317 (54), 316 (15), 315 (3%).

**2,7-Di-*tert*-butyl-1-nitropyrene-4,5,9,10-*d*<sub>4</sub>.** A suspension of 2.30 g (7.22 mmol) of 6 in 100 mL of acetic acid was heated to ~110 °C with stirring to give a homogeneous solution. After 0.53 mL of concd HNO<sub>3</sub> (d 1.38) was added in one portion, the resulting orange solution was heated at 110–117 °C for 1.5 h with stirring and poured into a large excess of ice-water. The orange powdery product was collected by filtration, washed with water, and dissolved in 100 mL of dichloromethane. The dichloromethane solution was washed with 1 N NaOH and then water and dried (MgSO<sub>4</sub>). After evaporation, the residue was chromatographed on silica gel with 1:5 benzene-hexane to give pure 2,7-di-*tert*-butyl-1-nitropyrene-4,5,9,10-*d*<sub>4</sub> in 89% yield (2.34 g, 6.4 mmol). Crystallization from hexane-benzene gave yellow prisms with mp 173–174 °C: <sup>1</sup>H NMR (CDCl<sub>3</sub>) 1.58 (s, 9 H), 1.64 (s, 9 H), 8.26 (d,  $J = 1.9$  Hz, 1 H), 8.27 (s, 1 H), 8.28 (d,  $J = 1.9$  Hz, 1 H).

**1-Amino-2,7-di-*tert*-butylpyrene-4,5,9,10-*d*<sub>4</sub>.** A solution of 1.80 g (4.95 mmol) of 2,7-di-*tert*-butyl-1-nitropyrene-4,5,9,10-*d*<sub>4</sub> in 72 mL of absolute methanol and 14 mL of benzene was refluxed over 104 g of 4.4% of sodium amalgam for 12–15 h. The organic layer was poured into a large excess of ice-water, separated, dried (MgSO<sub>4</sub>), and evaporated, and the residue was chromatographed on silica gel with 1:1 benzene-hexane to give almost pure 1-amino-2,7-di-*tert*-butylpyrene-4,5,9,10-*d*<sub>4</sub> in 72% yield (1.19 g, 3.57 mmol). Crystallization from hexane-benzene gave yellow plates with mp 255–257 °C: IR (KBr) 3500 and 3400 (NH<sub>2</sub>), 2950 cm<sup>-1</sup> (*t*-Bu); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.56 (s, 9 H), 1.67 (s, 9 H), 4.10 (br s, 2 H), 7.88–8.08 (m, 3 H); MS (70 eV)  $m/z$  (relative intensity) 335 (9), 334 (28), 333 (M<sup>+</sup>, 100), 332 (53), 331 (13), 330 (3%).

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***N*-[(4-Nitrophenyl)thio]-1-amino-2,7-di-*tert*-butylpyrene-4,5,9,10-*d*<sub>4</sub> (7).** To a stirred solution of 0.30 g (0.90 mmol) of 1-amino-2,7-di-*tert*-butylpyrene-4,5,9,10-*d*<sub>4</sub> and 0.5 mL of triethylamine in 50 mL of dry THF was added dropwise at 0 °C a solution of 0.86 g (4.5 mmol) of 4-nitrobenzenesulfonyl chloride in 10 mL of dry THF. After being stirred for 2 h at 0 °C, the reaction mixture was filtered and evaporated under reduced pressure, and the residue was chromatographed on alumina (Merck, aluminium oxide 90) with 1:1 hexane-benzene as eluant. Crystallization from hexane-benzene gave **7** as orange microprisms with mp 181–183 °C in 27% yield (0.116 g, 0.24 mmol): IR (KBr) 3360 (NH), 2950 (t-Bu), 2250 cm<sup>-1</sup> (C–D); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.54 (s, 9 H), 1.75 (s, 9 H), 5.94 (s, 1 H), 7.76 (d, *J* = 9.3 Hz, 2 H), 8.09 (d, *J* = 1.9 Hz, 1 H), 8.14 (d, *J* = 1.9 Hz, 1 H), 8.15 (s, 1 H), 8.34 (d, *J* = 9.3 Hz, 2 H). Anal. Calcd for C<sub>30</sub>H<sub>26</sub>D<sub>4</sub>N<sub>2</sub>O<sub>2</sub>S: C, 74.04; H, 6.21; N, 5.76. Found: C, 73.77; H, 6.25; N, 6.00.

***N*-[(4-Nitrophenyl)thio]-2,7-di-*tert*-butyl-1-pyrenylaminy-4,5,9,10-*d*<sub>4</sub> Radical (3).** Precursor **7** (0.100 g, 0.205 mmol) was dissolved in 20 mL of benzene with stirring. After 0.90 g of K<sub>2</sub>CO<sub>3</sub> was added, 0.90 g of PbO<sub>2</sub> 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. This left a dark-red crystalline powder, which was heated in 1 mL of benzene at the reflux temperature for ~1 min, and then 20 mL of hexane was added. Upon cooling at 0 °C overnight, **3** was obtained as reddish black fine needles in 27% yield (27 mg, 0.055 mmol): mp 188–190 °C; IR (KBr) 2950, 2250, 1590, 1570, 1515, 1470, 1330, 1160, 1110, 1080, 875, 855, 835, 810, 740, 660 cm<sup>-1</sup>. Anal. Calcd for C<sub>30</sub>H<sub>25</sub>D<sub>4</sub>N<sub>2</sub>O<sub>2</sub>S: C, 74.19; H, 6.02; N, 5.77. Found: C, 73.90; H, 6.09; N, 5.58.

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