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Preparation and Isolation of an Exceptionally Persistent Nitrogen-centered Free Radical. *N*-[(4-Nitrophenyl)thio]-2,7-di-*t*-butyl-1-pyrenylaminyl[1)]

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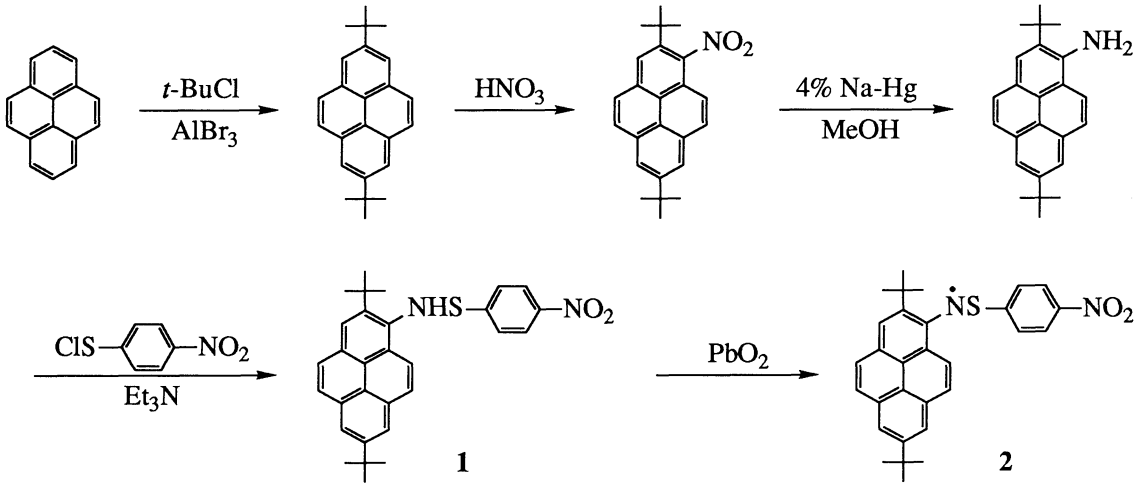
Oxidation of *N*-[(4-nitrophenyl)thio]-2,7-di-*t*-butyl-1-aminopyrene yields an exceptionally persistent and oxygen-insensitive *N*-[(4-nitrophenyl)thio]-2,7-di-*t*-butyl-1-pyrenylaminyl, which has been isolated as pure radical crystals in 31% yield. The crystals can be stored, without decomposition, for a long period.

Radical persistence is a function of electronic stabilization and steric protection. Thioaminyls (RNSR') are electronically highly stabilized by the conjugative delocalization of the unpaired electron from the nitrogen to the sulfur (-$\dot{N}$-$\ddot{S}$- ⟷ -$\ddot{N}$-$\dot{S}$-).[2)] In previous papers we reported that some sterically protected thioaminyls can be isolated as pure radical crystals.[3,4)] The recent chemistry of stable free radicals has been largely stimulated by the suggestion that polyradicals might be possible organic ferromagnets.[5)] However, in spite of much effort to obtain novel stable free radicals, they remain still very rare.[6)]

In the course of the ESR studies on thioaminyls we found that *N*-[(4-nitrophenyl)thio]-2,7-di-*t*-butyl-1-pyrenylaminyl (**2**), generated by oxidation of *N*-[(4-nitrophenyl)thio]-2,7-di-*t*-butyl-1-aminopyrene (**1**), is very stable and oxygen-insensitive in solution. Herein we report preparation and isolation of **2**, and the ESR spectrum.

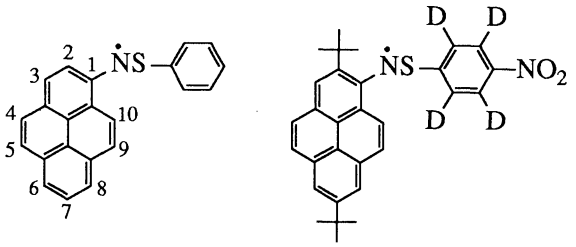


Scheme 1.

Precursor **1** was prepared by the route outlined in Scheme 1. 2,7-Di-*t*-butyl-1-nitropyrene was obtained by the reported method.[7] Reduction of the nitropyrene was performed with 4% Na - Hg in methanol, giving 2,7-di-*t*-butyl-1-aminopyrene in 50% yield. The reaction of the aminopyrene with 4-nitrobenzenesulfenyl chloride in the presence of triethylamine gave **1** in 40% yield. Oxidation of **1** was performed with PbO_2. When PbO_2 was added to a stirred solution of **1** and K_2CO_3 in benzene, the light yellow solution was immediately turned red and gave an intense ESR signal with a *g* value of 2.0043 (Fig. 1).

The ESR spectrum of **2** is very complex due to the interaction of the unpaired electron with many magnetically inequivalent protons. The spectrum was therefore analyzed by the computer simulation method. As found in Fig. 1, the experimental ESR spectrum is satisfactorily reconstructed by using the following hyperfine coupling (hfc) constants: a_N = 0.664, a_H (1H) = 0.363, 0.316, 0.302, 0.298, 0.152, 0.150, 0.126, a_H (2H) = 0.041 mT. The Huckel and McLachlan-Huckel molecular orbital calculations [8] for **3**, performed assuming that the radical is planar, predict that the spin densities on C2, C5, C6, C8, and C9 are much higher than those on C3, C4, C7, and C10. Accordingly, it is likely that the protons giving the large hfc constants of 0.363, 0.316, 0.302, and 0.298 mT are those attached to C5, C6, C8, and C9. Furthermore, we confirm that the proton hfc constant of 0.041 mT is due to the ortho protons of the phenylthiyl group from the ESR spectrum of the radical, *N*-[(4-nitrophenyl-d_4)thio]-2,7-di-*t*-butyl-1-pyrenylaminyl (**4**) giving the following parameters: a_N = 0.664, a_H (1H) = 0.364, 0.317, 0.302, 0.298, 0.151, 0.133, 0.126 mT (in benzene at 20 °C).

Radical **2** is exceptionally persistent in solution, even in the presence of oxygen. This is clearly shown by Fig. 2. Although a solution of **2** in benzene was placed in an open (not sealed) ESR cell and the intensities of the ESR signals from the solution



3 **4**

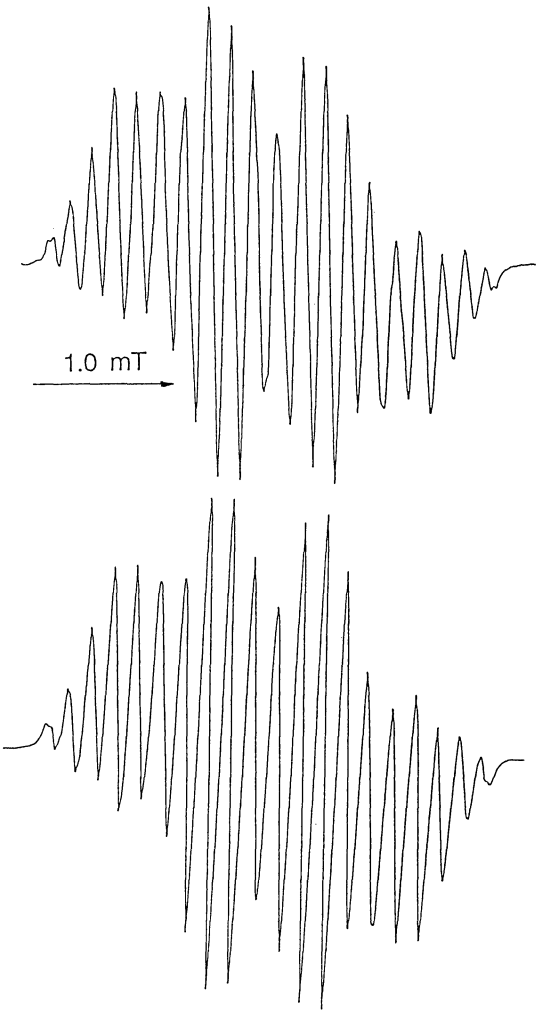


Fig. 1. Experimental ESR spectra of **2** (top) in benzene at 20 °C and a computer-simulated ESR spectrum (bottom) reconstructed by using the hfc constants shown in the text.

were followed at 21 °C over 5 h by ESR spectroscopy, no reduction in the intensities of the ESR spectra was found during the experimental period. Furthermore, it was found that **2** in solution showed no tendency to dimerize, even on cooling to low temperatures (≈ - 50 °C). From these observations it has been concluded that **2** is exceptionally persistent, even in the presence of oxygen, and exist solely as individual radicals in solution. These results prompted us to isolate **2** as radical crystals.

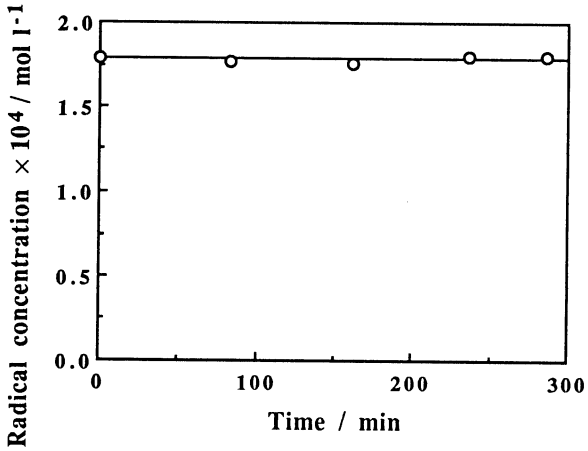


Fig. 2. Radical stability of **2** in benzene at 20 °C in the presence of oxygen.

Isolation was performed as follows: a benzene solution of **1** 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 hexane benzene to give **2** as reddish black microneedles with mp 190 - 192 °C in 31% yield. The structure was confirmed by the IR spectrum showing no NH absorption and the satisfactory elemental analysis.[9] Interestingly, no decomposition of **2** was found on heating radical **2** in a refluxing benzene for 5 h. This observation indicates that **2** is thermally very stable. Furthermore, it was found that crystals of **2** can be stored, without decomposition, over a long period at 0 °C.

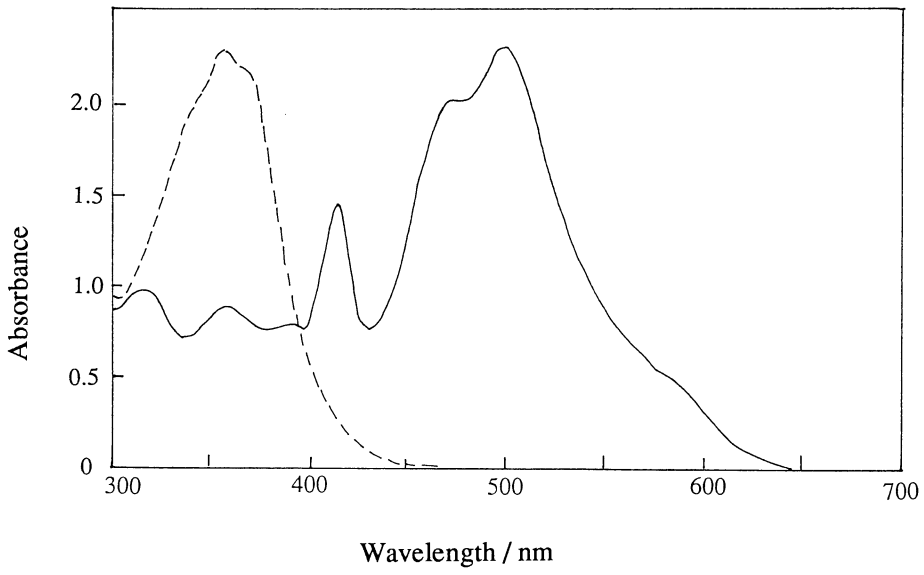


Fig. 3. UV - vis spectra of **1** and **2** in benzene: **1** (——) 8.19×10^{-5} mol l^{-1}; **2** (------) 9.20×10^{-5} mol l^{-1}.

Radical **2** gives interesting differences in comparison of the hfc constants and *g* value with other thioaminyl radicals. The large a_H values (0.363 - 0.126 mT) due to the protons of the pyrenyl ring indicate that, in **2**, the unpaired electron is largely delocalized onto the pyrenyl ring. Accordingly, the spin densities on the nitrogen (central) and phenylthiyl group are considerably reduced. This is clearly shown by comparison of the a_N and a_H values (due to the ortho protons of the phenylthiyl group) with those (a_N = 0.959; a_H = 0.078 mT) for PhNSPh radical.[10] For a_N, the reduction in the magnitude is indeed 0.295 mT, and for a_H, that is 0.037 mT. The reduced *g* value (2.0043) for **2** (2.0059 for PhNSPh)[10] can also be accounted for in the same manner; that is, the spin density on the sulfur having a large spin - orbit coupling parameter ($382cm^{-1}$)[11] is considerably reduced by the delocalization of the unpaired electron onto the pyrenyl ring.

A UV-vis spectrum of **2** is illustrated in Fig. 3. Radical **2** is characterized by the dark red color. As found in the UV-vis spectrum, **2** has absorption peaks at 497 (ε 25500), 471 (22300), and 412 nm (16000) in the visible region and at 387 (ε 8830), 359 (9910), and 318 nm (10700) in the UV region. Owing to the strong absorption at 497 nm the radical shows a characteristic red color. When solvents and reagents used do not have absorptions in the visible region, one can readily determine the concentrations of **2** by measuring the absorbance at 497 nm.

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8) $\alpha_N = \alpha + 0.6\beta$, $\alpha_S = \alpha + \beta$, $\beta_{CN} = 1.1\beta$, $\beta_{NS} = 0.7\beta$, $\beta_{CS} = 0.7\beta$, $\lambda = 0.7$.
9) IR (KBr): 2930, 1565, 1510, 1465, 1330, 1220, 1160, 1100, 1070, 850, 810, 730 cm^{-1}. Anal. Found: C, 74.98; H, 6.07; N, 5.76%. Calcd for $C_{20}H_{29}N_2O_2S$: C, 74.81; H, 6.07; N, 5.82%.
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