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Generation, ESR Spectra, and Isolation of *N*-(Arylthio)-4-*t*-butyl-2,6-diphenylphenylaminyl Radicals[1)]

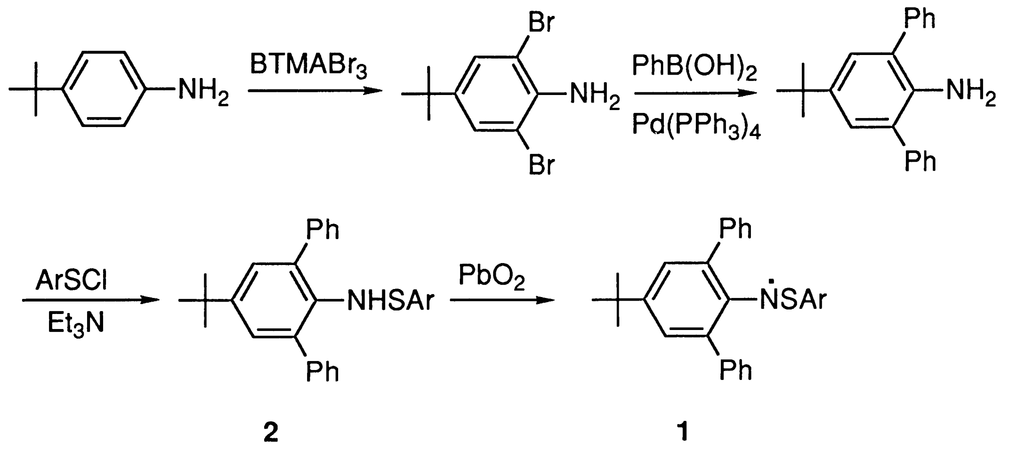
Yozo MIURA,* Tomohiro FUCHIKAMI, and Masayoshi MOMOKI
Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558

Oxidation of *N*-(arylthio)-4-*t*-butyl-2,6-diphenylanilines yields quite persistent and oxygen-insensitive *N*-(arylthio)-4-*t*-butyl-2,6-diphenylphenylaminyls which, in solution, give a characteristic blue, purple, or wine-red color. Among the aminyls generated, *N*-(4-nitrophenylthio)-4-*t*-butyl-2,6-diphenylphenylaminyl is isolated as radical crystals. The ESR spectra are split into a simple 1 : 1 : 1 triplet by the interaction with a nitrogen nucleus. Upon deuteration of the phenyl groups at the 2 and 6 positions of the anilino group, the 1:1:1 triplets are split further by the interaction with the meta protons of the anilino group and the ortho protons of the arylthio group. The spin density distribution in the radical is discussed on the basis of the hyperfine coupling constants.

Isolable stable free radicals have attracted widely increasing interest from the viewpoints of both pure and applied chemistry because of the expectation that radical crystals might behave as purely molecular-based magnetic materials.[2)] However, the advance in this field have seriously been limited because of the unavailability of isolable stable free radicals. We have therefore searched for exceptionally persistent free radicals.

Radical persistence is a function of electronic stabilization and steric protection. Thioaminyl radicals (RNSR') are electronically greatly stabilized by the conjugative delocalization of the unpaired electron from the nitrogen to the sulfur $(\text{-}\dot{\mathrm{N}}\text{–}\ddot{\mathrm{S}}\text{-} \longleftrightarrow \text{-}\overset{-}{\ddot{\mathrm{N}}}\text{–}\overset{+}{\dot{\mathrm{S}}}\text{-})$. If the reactive positions of high spin density are sufficiently protected from the reversible or irreversible homolytic reactions to destroy the radicals, the aminyls may be isolated in the radical form. Along this line, a variety of thioaminyl radicals have been prepared and their spin density distributions and stabilities have been evaluated.[3)] It has been found that *N*-[(4-nitrophenyl)thio]-2,4,6-tri-*t*-butylphenylaminyl,[4)] *N*-(arylthio)-2,4,6-triphenylphenylaminyl,[5)] and *N*-[(4-nitrophenyl)thio]-2,7-di-*t*-butyl-1-pyrenylaminyl[6)] can be isolated as pure radical crystals. In the extension of our ESR study on thioaminyl radicals, we recently found that *N*-(arylthio)-4-*t*-butyl-2,6-diphenylaminyls (**1**) are quite persistent and oxygen insensitive radicals. In this communication we report generation, ESR spectra, stabilities, and isolation of **1**.

Precursors *N*-(arylthio)-4-*t*-butyl-2,6-diphenylanilines (**2**) were prepared according to the route shown in Fig. 1. Upon treatment of 4-*t*-butylaniline with benzyltrimethylammonium tribromide (BTMABr$_3$) in dichloromethane-methanol in the presence of CaCO$_3$ gave 4-*t*-butyl-2,6-dibromoaniline in 90% yield.[7)] The dibromo compound was then allowed to react with two equivalents of phenylboric acid using Pd(PPh$_3$)$_4$ as a catalyst to yield 4-*t*-butyl-2,6-diphenylaniline in 92% yield.[8)] The aniline was treated with benzenesulfenyl chlorides in dry ether in the presence of triethylamine to give **2** in 11 - 36% yield after column chromatographic separation and subsequent crystallization.



a: Ar = 4-ClC_6H_4 **c**: Ar = 3-$NO_2C_6H_4$
b: Ar = 4-BrC_6H_4 **d**: Ar = 4-$NO_2C_6H_4$

Scheme 1.

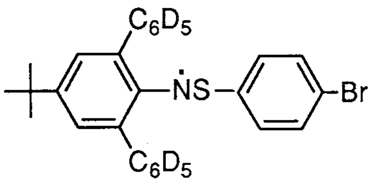
Generation of **1**was accomplished by PbO_2 oxidation of **2**. When PbO_2 was added to a solution of **2** in benzene, a colorless or light yellow solution immediately turned blue (**1a, 1b**), purple (**1c**), or wine-red (**1d**) and gave an intense ESR signal consisting of a 1 : 1 : 1 triplet with quite poorly resolved splittings due to aromatic protons (Fig. 1). This line broadening is ascribed to the presence of many unresolved aromatic protons.

Aminyls **1** were quite persistent, even in the presence of atmospheric oxygen. This was shown by brief kinetic ESR measurements. A benzene solution of **1** was put into an open ESR cell and double integrated ESR signals were measured for 10 h at room temperature (20 °C) under atmospheric conditions. Interestingly, during the measurements no or negligibly small reduction in the ESR signal intensities was observed, indicating that aminyls **3** are quite persistent and oxygen-insensitive radicals. Furthermore, even upon cooling to -50 °C in solution, radicals exhibited no tendency to dimerize, indicating that they exist as the individual radicals. These interesting results prompted us to isolate them.

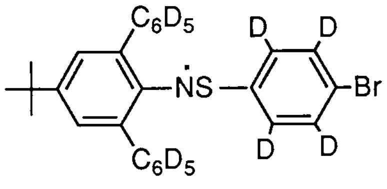
Isolation was accomplished as follows. Precursors of **2a** - **d** were treated with PbO_2 in benzene in the presence of K_2CO_3. After filtration, the solvent was removed by freeze-drying and the resulting micro crystalline residue was recrystallized from hexane. Among **1a** - **d**, **1d** could be isolated as dark brown prisms with mp 140 - 142 °C. The structure was confirmed by the satisfactory elemental analyses[9] and the IR spectrum which shows no NH absorption (in the IR spectra of **2d** a strong absorption peak due to the stretching vibration of the N-H is observed at 3300 cm^{-1}). The spin concentration of **1d** was determined by ESR to be ~100%.[10] The radical crystals were stable for a long period without decomposition upon storage at 0 °C in the dark.

Aminyls **1** in solution show a characteristic blue, purple, or wine-red color. In a UV-visible spectrum of **1d** it gives absorption peaks at 583 (ε 6000) and 492 nm (9690) in the visible region and at 387 (12500) and 309 nm (11300) in the UV region. On the other hand, **1a**, **1b**, and **1c** in benzene show absorption peaks at 549 and 520 (sh), 595 and 522 (sh), and 579 and 501 nm, respectivly, in the visible region.

Upon deuteration of the phenyl groups at the 2 and 6 positions of the anilino group (**3a** and **3b**), the peak-to-peak line widths in the ESR spectra became very small (< 0.07 mT), and the hyperfine couplings due to the anilino meta and arylthio ortho protons were clearly observed, as found in Fig. 2. From the ESR spectra of **3a** and **3b** the hyperfine coupling (hfc) constants due to the anilino meta and phenylthio ortho protons were unequivocally determined to be 0.130 and 0.085 mT, respectively. Furthermore, in the ESR spectrum of **3b** satellite lines due to ^{33}S at natural abundance (0.76%), together with satellite lines due to ^{13}C at natural abundance (1.11%), could be detected in both wings where the spectrum was recorded at high gain (100 times). The assignments of the satellite lines were performed by the intensity ratios [^{33}S: experimental 0.13% (theoretical 0.19%; ^{13}C: experimental 0.40% (theoretical 0.55%)] of the satellite lines appearing in the left wing to the parent spectrum. The ESR parameters for **1** and **3** are summarized in Table 1.



3a



3b

Table 1. ESR Parameters for **1** and **3** in Benzene at 20 °C

Radical	a_N / mT	$a_{other}$$^{a)}$/ mT	g
1a	0.934		2.0058
1b	0.933		2.0060
1c	0.936		2.0055
1d	0.932		2.0055
3a	0.932	0.130 (2H),$^{b)}$ 0.085 (2H),$^{c)}$	2.0060
3b	0.934	0.130 (2H)$^{b)}$, 0.51 (^{33}S), 1.01 (1^{13}C)	2.0060

a) The numbers in parentheses refer to the number of equivalent nuclei. b) The value for the anilino meta protons. c) The value for the phenylthio ortho protons.

It is obvious from Table 1 that the unpaired electron is extensively delocalized onto the anilino and arylthio group. If 2.2 and 2.3 mT are adopted for Q_N and Q_{33S} of McConnell's equation ($a_X = Q_X\rho_X$),[11] the spin densities on N and S are derived to be 0.42 and 0.22, respectively. Hence, the high g values for **1** and **3** can be accounted for in terms of the high spin density on the sulfur which has a high spin-orbit coupling parameter (382 cm^{-1}).[12]

On the basis of the results obtained in this work, the following conclusions are drawn. (1) Aminyls **1** are quite persistent and oxygen-insensitive radicals; (2) aminyl **1d** can be isolated as radical crystals, which are stable for a long period without decomposition upon storage at 0 °C in the dark; (3) the unpaired electron is extensively delocalized over the whole of the radicals.

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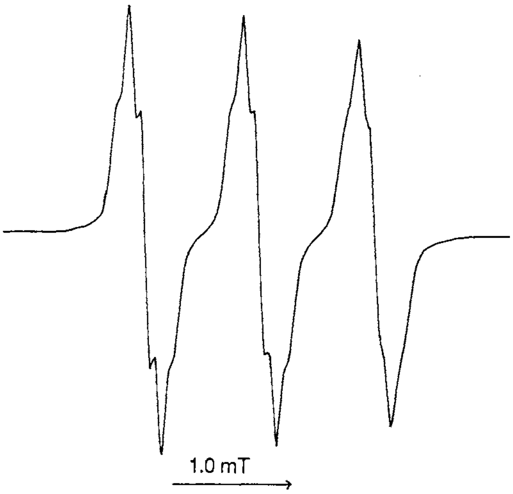

Fig. 1. ESR spectrum of **1b** in benzene at 20 °C.

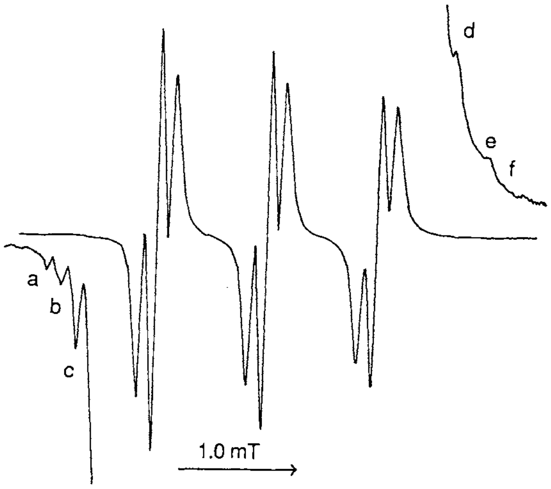

Fig. 2. ESR spectrum of **3b** in benzene at 20 °C. Both wings are recorded at high gain (100 times). a, b, e, and f: satellite lines due to ^{33}S isotope; c and d: satellite lines due to ^{13}C isotope.

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9) Found: C, 73.87; H, 5.41; N, 6.23%. Calcd for $C_{28}H_{25}N_2O_2S$: C, 74.14; H, 5.56; N, 6.18%.
10) The spin concentration of **1d** was determined by double integration of ESR spectra of **1d** in benzene. The calibration curve was drawn with 1,3,5-triphenylverdazyl using the same ESR cell and solvent and the same instrument settings as for the sample measurements.
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