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ESR Spectroscopic Study of Triphenylmethyl-Substituted Thioaminyl Radicals: *N*-(Triphenylmethylthio)alkylaminyls and -arylaminyls[1)]

Yozo Miura,* Mamoru Isogai, and Masayoshi Kinoshita
Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558

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Synopsis. The title radicals, generated by hydrogen-atom abstraction from the corresponding *N*-(triphenylmethylthio)-alkylamines and -arylamines, have been studied by means of ESR spectroscopy. The alkylaminyls were transient in solution at room temperature, while the arylaminyls persisted for a long period under the same conditions. The ESR parameters are discussed by comparing them with those for structurally related aminyls.

Thioaminyl radicals ($R\dot{N}SR'$) have an interesting structure in which a divalent sulfur atom attaches directly to the radical center. In our ESR studies of a variety of thioaminyl radicals, we have found that, in the radicals, the unpaired electron is delocalized considerably onto the adjacent sulfur and that some thioaminyls can be isolated as hydrazine-like dimers or pure radical crystals.[2,3)] In the present paper we wish to report an ESR spectroscopic study of *N*-(triphenylmethylthio)alkylaminyls and -arylaminyls (**2**), which have never appeared in the literature.[4)]

Results and Discussion

Thioaminyls **2** were generated by the phtolysis of *N*-(triphenylmethylthio)alkylamines or -arylamines (**1**) in benzene in the presence of di-*t*-butyl peroxide. Additionally, the arylaminyls **2d** and **2e** were also generated by treating the corresponding amines with (*t*-BuOOCO-)$_2$. Some typical ESR spectra are illustrated in Figs. 1 and 2, while the ESR parameters are summarized in Table 1.

Although the radical generation was performed at room temperature with a low-power mercury lamp (100 W), all the ESR spectra were relatively strong, as may be found in Fig. 1. However, upon the interruption of UV-irradiation, the ESR signals due to the alkylaminyls **2a**—**c** disappeared immediately at room temperature. On the other hand, the arylaminyls **2d** and **2e** survived for a long period under the same conditions; in particular, **2e** was quite long-lived; the lifetime shown by a brief kinetic study was more than a week.

In most spectra, an impure radical with a *g* value of 2.003 appeared in the signals of **2**, as is shown in Fig. 1. The low *g* value and its extremely persistent property suggested that the impure radical was the triphenylmethyl radical. This was confirmed by comparing its ESR spectrum with that of an authentic triphenylmethyl radical obtained from a solution of $PhN{=}NCPh_3$. This impure radical was not observed from the pho-

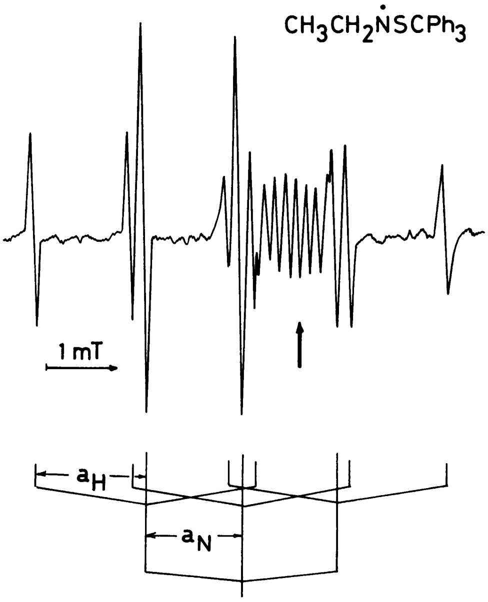


Fig. 1. ESR spectrum of **2b** recorded during photolysis of a solution of **1b** in 1:4 (v/v) di-*t*-butyl peroxide-benzene at 17 °C. The impure radical indicated by a bold arrow is the triphenylmethyl radical.

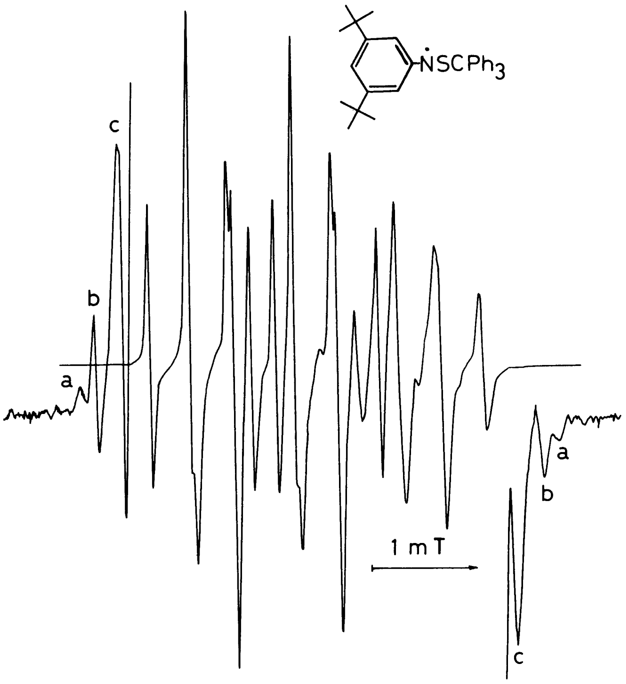
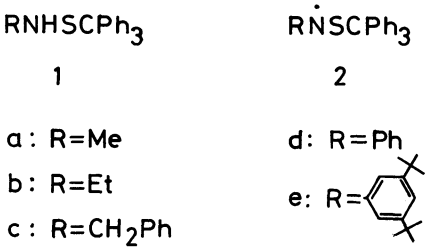


Fig. 2. ESR spectrum of **2e** generated by treating **1e** with (*t*-BuOOCO-)$_2$ in degassed benzene at 17 °C. Both wings of the parent signal are shown at high gain (100 times). Assignment of the satellite lines are as follows: a, ^{33}S; b, ^{13}C (1C); c, ^{13}C (3C).

Table 1. ESR Parameters for *N*-(Triphenylmethylthio)alkylaminyls and -arylaminyls[a–c]

Radical	a_N	a_H[d]	g
2a	1.26	1.66 (3)	2.0074
2b	1.25	1.42 (2)	2.0073
2c	1.23	1.48 (2)	2.0073
2d[e]	0.995	0.381 (2),[f] 0.128 (2),[g] 0.426 (1)[h]	2.0062
2e[e,i]	0.988	0.385 (2),[f] 0.443 (1)[h]	2.0062

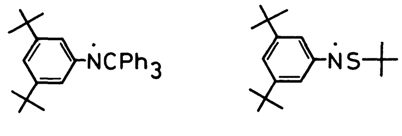
a) Hyperfine splitting constants are given in mT. b) Solvent: benzene or 1:4 (v/v) di-*t*-butyl peroxide-benzene. c) Temperature: 17±2 °C. d) Numbers in parentheses refer to the number of equivalent protons. e) Hyperfine splitting constants have been determined by computer simulation. f) Ortho protons on the anilino benzene ring. g) Meta protons on the anilino benzene ring. h) Para proton on the anilino benzene ring. i) $a_{^{13}C}$=0.55 (3C), 1.03 mT (1C), $a_{^{33}S}$=0.43 mT.



Scheme 1.

$$\mathrm{R\dot{N}SCPh_3} \longrightarrow \mathrm{RN{=}S} + \mathrm{Ph_3C\cdot}$$

Scheme 2.



3 5

Scheme 3.

tolysis of a solution of **1** alone. Thus, we thought that it was derived from **2**, probably through the homolytic C-S bond cleavage, as is shown in Scheme 2. A similar decomposition reaction of radicals has been reported to occur in aryl triphenylmethyl nitroxide radicals.[5]

Because of its considerably persistent property, the thioaminyl **2e** permitted us to measure some satellite lines due to ^{13}C and ^{33}S atoms at natural abundance (^{13}C 1.11%, ^{33}S 0.76%). As is shown in Fig. 2, three satellite lines were found in each wing of the parent spectrum recorded at a high gain (100 times). From the intensity ratios to the parent spectrum the a peak (<0.2%)[6] was assigned to the satellite lines due to ^{33}S, while the b (0.5%) and c peaks (1.3%) were assigned to those due to one and three magnetically almost equivalent ^{13}C atoms.

Furthermore, *N*-(triphenylmethyl)-3,5-di-*t*-butylphenylaminyl (**3**) was generated, for a comparison of the ESR parameters, by the oxidation of *N*-(triphenylmethyl)-3,5-di-*t*-butylaniline (**4**) with PbO_2. The ESR parameters thus obtained (in benzene at 17 °C) were a_N=0.931, $a_{o\text{-}H}$=0.563 (2H), $a_{p\text{-}H}$=0.727 mT (1H), and g=2.0038. This aminyl was relatively persistent and gave a strong ESR signal.

ESR Parameters. The aminyls **2** give ESR parameters very similar to those for the radicals of the $\mathrm{R\dot{N}SBu}^t$[2] and $\mathrm{Ar\dot{N}SBu}^t$[7] types (R=alkyl, Ar=aryl). For instance, the hyperfine splitting (hfs) constants for **2a** are very close to those for $\mathrm{Me\dot{N}SBu}^t$ (a_N=1.25, a_β=1.64 mT).[2] Similarly, those for **2e** are very similar to those for **5** (a_N=0.993, $a_{o\text{-}H}$=0.368, $a_{p\text{-}H}$=0.420, $a_{^{33}S}$=0.466 mT).[2,7] Accordingly, we can say that the thioaminyls **2** adopt the same, or almost the same, configuration as the $\mathrm{R\dot{N}SBu}^t$ or $\mathrm{Ar\dot{N}SBu}^t$ radicals (probably planar around the nitrogen).[2]

In contrast, the ESR parameters are quite different from those of the radicals of the $\mathrm{R\dot{N}R'}$ or $\mathrm{Ar\dot{N}R}$ type radicals.[8] A typical example is given by **3**, whose $a_{o\text{-}H}$ and $a_{p\text{-}H}$ values are substantially higher than those for **2e**. The reduction in a_H found in going from **3** to **2e** is obviously a consequence of the conjugative delocalization of the unpaired electron from the nitrogen to the sulfur in **2** ($\mathrm{-\dot{N}\text{-}\ddot{S}\text{-}} \leftrightarrow \mathrm{-\ddot{N}^{-}\text{-}\dot{S}^{+}\text{-}}$), as is suggested by the relatively high $a_{^{33}S}$ value and the higher *g* value. Here, the π-orbital spin density (ρ_S^π) on the sulfur in **2e** was estimated from the $a_{^{33}S}$ value by using Equation 1, which had been previously established through an investigation of the ^{33}S hfs constants of a variety of $\mathrm{R\dot{N}SR'}$ radicals.[2] The ρ_S^π value thus obtained is 0.18;

$$\rho_S^\pi = a_{^{33}S}/Q_S = a_{^{33}S}/2.3\ \mathrm{mT} \qquad (1)$$

this magnitude strongly suggests that the thioaminyls **2** are electronically substantially stabilized by this conjugation. However, because of the relatively weak C-S bonds, the thioaminyls **2** were less persistent than had been anticipated, and no **2** could be isolated as the radical or dimer substance.

Experimental

The melting points and the IR and ^1H NMR spectra were taken as previously reported.[9] Triphenylmethanesulfenyl chloride[10] (Ph_3CSCl), phenylazotriphenylmethane,[11] and 3,5-di-*t*-butylaniline[12] were prepared by the previously reported methods.

The *N*-(triphenylmethylthio)amines (**1**) were prepared by either method, A or B. Method A: a solution of 1.12 g (3.60 mmol) of Ph_3CSCl in 15 ml of CH_2Cl_2 was added dropwise to an aqueous RNH_2 solution (with a large excess of RNH_2) with vigorous stirring at 0 °C. After being stirred for 0.5 h at the same temperature, the organic layer was separated and dried over $MgSO_4$. After filtration, the solvent was evaporated, and the residue was chromatographed on silica gel (Wako gel C-200; column size 4×20 cm) using 1 : 2 (v/v) benzene-hexane as the eluant and was crystallized from methanol.

Method B: a solution of 1.12 g (3.60 mmol) of Ph_3CSCl in 15 ml of CH_2Cl_2 was added dropwise to a solution of 10 mmol of RNH_2 (or 4.5 mmol of RNH_2 and 7.2 mmol of Et_3N) in 10 ml of CH_2Cl_2 with stirring at 0 °C. After being stirred for 1 h at the same temperature, the reaction mixture was washed with water (30 ml×3), saturated K_2CO_3 (30 ml), and brine (30 ml), and dried over $MgSO_4$. After filtration, the solvent was evaporated, and the residue was chromatographed as above and crystallized from methanol.

N-(Triphenylmethylthio)methylamine (**1a**) [mp 109—111 °C (lit,[13] 119—120 °C)] and *N*-(triphenylmethylthio)ethylamine (**1b**) were obtained by Method A, while *N*-(triphenylmethylthio)benzylamine (**1c**), *N*-(triphenylmethylthio)aniline (**1d**) [mp 96—98 °C (lit,[13] 103 °C)], and *N*-(triphenylmethylthio)-3,5-di-*t*-butylaniline (**1e**) were prepared by Method B.

Thioamine 1b: Colorless prisms; mp 88—90 °C yield 47% (0.54 g, 1.7 mmol); IR (KBr) 3260 cm^{-1} (NH); ^1H NMR ($CDCl_3$) δ=0.82 (t, J=7 Hz, 3H, CH_3), 2.40 (s, 1H, NH), 2.52 (q, J=7 Hz, 2H, CH_2), 7.12—7.42 (m, 15H, aromatic). Found: C, 79.26; H, 6.64; N, 4.44%. Calcd for $C_{21}H_{21}NS$: C, 78.95; H, 6.63; N, 4.38%.

Thioamine 1c: Colorless needles; mp 97—98 °C; yield 61% (0.82 g, 2.2 mmol); IR (KBr) 3300 cm^{-1} (NH); ^1H NMR ($CDCl_3$) δ=2.72 (t, J=5.9 Hz, 1H, NH), 3.62 (d, J=5.9 Hz, 2H, CH_2), 6.92—7.48 (m, 20H, aromatic). Found: C, 81.91; H, 6.13; N, 3.56%. Calcd for $C_{26}H_{23}NS$: C, 81.85; H, 6.08; N, 3.67%.

Thioaniline 1e: Pale yellow prisms; mp 117—119 °C yield 26% (0.45 g, 0.93 mmol); IR (KBr) 3350 cm^{-1} (NH); ^1H NMR ($CDCl_3$) δ=1.19 (s, 18H, *t*-Bu), 4.78 (s, 1H, NH), 6.49—7.42 (m, 18H, aromatic). Found: C, 82.24; H, 7.72; N, 2.82; S, 6.90%. Calcd for $C_{33}H_{37}NS$: C, 82.62; H, 7.77; N, 2.92; S, 6.68%.

***N*-(Triphenylmethyl)-3,5-di-*t*-butylaniline (4).** A mixture of 0.80 g (3.9 mmol) of 3,5-di-*t*-butylaniline, 1.0 g (3.6 mmol) of triphenylmethyl chloride, and 1.5 ml of Et_3N in 50 ml of dry ether was stirred at room temperature for 24 h. After the reaction mixture was filtered and evaporated, the residue was crystallized from methanol to give pale yellow prisms in a 39% yield (0.62 g, 1.4 mmol). Mp 172.5—173.5 °C; IR (KBr) 3410 cm^{-1} (NH); ^1H NMR ($CDCl_3$) δ=1.06 (s, 18H, *t*-Bu), 4.85 (s, 1H, NH), 6.14—7.39 (m, 18H, aromatic). Found: C, 88.81; H, 8.42; N, 2.88%. Calcd for $C_{33}H_{37}N$: C, 88.54; H, 8.33; N, 3.13%.

ESR Measurements. Aminyls **2** were generated by the photolysis or **1** in degassed 1 : 4 di-*t*-butyl peroxide-benzene with a high-pressure mercury lamp. Aminyls **2d** and **2e** were also generated by treating the corresponding **1** with (*t*-BuOOCO-)$_2$ in degassed benzene. Radical **3** was prepared by the oxidation of **4** with PbO_2 in benzene. All the ESR spectra were recorded at 17±2 °C on a JEOL JES-ME-3X spectrometer. The hyperfine splitting constants and *g* values were determined by comparison with Fremy's salt in a K_2CO_3 aqueous solution (a_N=1.309 mT, g=2.0057).

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