

Isolation of Exceptionally Persistent Nitrogen-centred Free Radicals: *N*-Arylthio-2,4,6-triphenylanilino Radicals

Yozo Miura* and Akio Tanaka

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan

N-Arylthio-2,4,6-triphenylanilino radicals are exceptionally persistent and oxygen-insensitive in solution, allowing their isolation as pure radical crystals.

Although numerous free radicals have been generated by various methods, persistent radicals are rare;¹ in particular, radicals isolated in a pure form are very interesting and recently have attracted much attention in connection with organic ferromagnetic materials.² We have found that *N*-aryl-

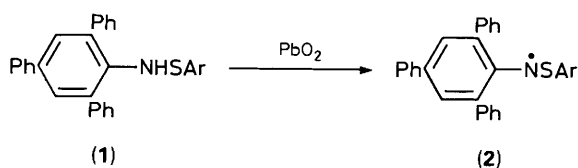
thio-2,4,6-triphenylanilino radicals (**2**) are exceptionally persistent and can be isolated as pure radical crystals. Herein we report the generation, ESR spectra, and isolation of (**2**).

Thioaminyls (**2**) were generated by oxidation of *N*-arylthio-2,4,6-triphenylanilines (**1**) with PbO₂ in the presence of

Table 1. ESR parameters and λ_{\max} for (2) in benzene at 21 °C.

Radical	Hyperfine splittings/mT		λ_{\max}/nm
	a_N	g	
(2a)	0.895	2.0057	637
(2b)	0.894	2.0059	637
(2c)	0.895	2.0055	638
(2d)	0.891	2.0054	628
(3) ^{a,b}	0.959	2.0059	

^a Ref. 4. ^b The other hyperfine splitting constants (in mT) are: 0.370 (*o*-H of PhN⁻); 0.126 (*m*-H of PhN⁻); 0.418 (*p*-H of PhN⁻); 0.078 (*o*-H of PhS⁻); 0.027 (*m*-H of PhS⁻); 0.084 (*p*-H of PhS⁻).



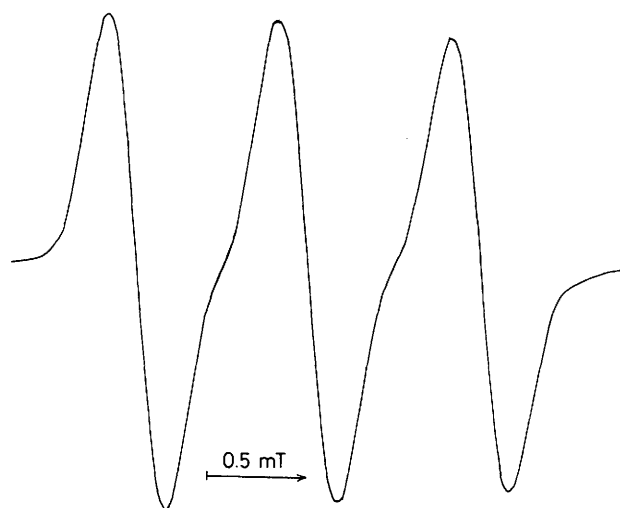
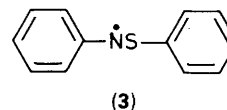
- a; Ar = *p*-ClC₆H₄
 b; Ar = *p*-BrC₆H₄
 c; Ar = 2,4-Cl₂C₆H₃
 d; Ar = 3,5-Cl₂C₆H₃

K₂CO₃. When PbO₂ was added to a stirred mixture of (1) and K₂CO₃ in benzene, the colourless mixture immediately turned dark bluish green and the resulting coloured solution gave an intense 1:1:1 triplet ESR spectrum due to (2). The ESR parameters and λ_{\max} for (2) are summarized in Table 1.

Thioaminyloxy radicals (2) were quite persistent, even in the presence of oxygen. This was shown by a brief kinetic ESR experiment; a solution of (2) (0.13 mmol/dm⁻³) in benzene was placed in an open ESR cell and the intensity of the ESR signal was followed at 21 °C for 6 h by ESR spectroscopy, but no reduction in the ESR signal intensity was detected. Furthermore, even on cooling to low temperatures in solution, (2) showed no tendency to dimerize. From these results we concluded that (2) is exceptionally persistent, even in the presence of oxygen, and exists solely as individual radicals in solution. These results prompted us to isolate (2) as radical crystals.

The isolation procedure was as follows. A benzene solution of (1) was stirred for *ca.* 5 min in the presence of PbO₂ and K₂CO₃. After filtration, the solvent was removed by freeze-drying and the resulting dark green crystalline powder was crystallized from hexane. In the case of (2c) pure dark purplish brown needles with m.p. 120–121.5 °C were given in ~50% yield. However, in the other cases no or only trace amounts of pure radical crystals were isolated. The structures of (2) were confirmed by their IR spectra, showing no N–H absorption, and satisfactory elemental analyses.

Thioaminyloxy radicals (RNSR[•]) generally are persistent radicals because they are stabilized electronically by conjugative delocalization of the unpaired electron from the nitrogen to the sulphur³ ($-\dot{\text{N}}-\ddot{\text{S}}- \longleftrightarrow -\dot{\text{N}}^--\dot{\text{S}}^+$). However, (3) is not so

**Figure 1.** ESR spectrum of (2a) in benzene at 21 °C.

long-lived⁴ since irreversible reactions occurring on the anilino benzene ring rapidly destroy it.⁵ The exceptional persistence of (2), therefore, can be explained primarily by both the electronic stabilization by the $-\dot{\text{N}}-\ddot{\text{S}}- \longleftrightarrow -\dot{\text{N}}^--\dot{\text{S}}^+$ conjugation and the steric protection by the three phenyl groups introduced to the anilino benzene ring.

As can be seen from Table 1, the a_N values for (2) are 0.061–0.069 mT lower than that for (3). This reduction in a_N is suggestive of delocalization of the unpaired electron onto the three phenyl groups attached to the anilino benzene ring. Therefore, the relatively broad lines in the ESR spectra of (2) [ΔH (peak to peak) 0.33 mT] can be accounted for in terms of many unresolved small hyperfine splittings due to the protons of the three phenyl groups.

Received, 15th December 1989; Com. 9/05342E

References

- A. R. Forrester, J. M. Hay, and R. H. Thomson, in 'Organic Chemistry of Stable Free Radicals,' Academic Press, London, 1968.
- Y. V. Korshak, T. V. Medvedeva, A. A. Ovchinnikov, and V. N. Spector, *Nature*, 1987, **326**, 370; M. Ota, S. Otani, and M. Igarashi, *Chem. Lett.*, 1989, 1183, and references cited therein.
- Y. Miura, H. Asada, M. Kinoshita, and K. Ohta, *J. Phys. Chem.*, 1983, **87**, 3450.
- Y. Miura and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1142; H. Sayo and K. Mori, *Chem. Pharm. Bull.*, 1977, **25**, 1489.
- Y. Miura, A. Yamamoto, and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 3215; L. Benati, P. C. Montevecchi, and P. Spagnolo, *J. Chem. Soc., Perkin Trans. 1*, 1982, 3049; C. Balboni, L. Benati, P. C. Montevecchi, and P. Spagnolo, *ibid.*, 1983, 2111.