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ELECTRON SPIN RESONANCE SPECTROSCOPIC INVESTIGATIONS OF t-BUTYL SUBSTITUTED N-ARYL-N-ARYLTHIOAMINYLS [1)]

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t-Butyl substituted N-aryl-N-arylthioaminyls (**2**) were generated and their ESR and visible spectral data were determined. The radicals persist for a few days and it seems that they are not sensitive to oxygen.

N-Aryl-N-arylthioaminyls (**2**) have been investigated in detail by electron spin resonance (ESR) spectroscopic method.[1)] The radicals are interesting in connection with (SN)x which has recently much attention as a superconductive polymer.[2,3)] The radicals, however, are not so long-lived as to permit to investigate their chemical properties, *e.g.*, the reactivity for the atmospheric oxygen, *etc*. Very recently, the present authors have found that the introduction of *t*-butyl groups into the N-phenyl ring of **2** makes **2** fairly persistent. This communication describes the chemical properties of **2**.

$$\underset{\mathbf{1}}{Ar_1\text{-NH-S-}Ar_2} \xrightarrow{\text{oxid.}} \underset{\mathbf{2}}{Ar_1\text{-}\dot{N}\text{-S-}Ar_2}$$

In a typical procedure, when 3',5'-di-*t*-butyl-4-chlorobenzenesulfenanilide (**1a**, 128 mg) was stirred in benzene (50 ml) in the presence of lead dioxide (3.0 g) and potassium carbonate (3.0 g), the solution immediately turned dark blue. After the reaction mixture was stirred for 15 minutes, the oxidizing agents were removed by filtration. It was found by ESR spectroscopic method that the blue solution contains N-3',5'-di-t-butylphenyl-N-4-chlorophenylthioaminyl (**2a**) in a concentration of 0.74 mmol/l. The value corresponds to 10% of the **1a** used. The blue color remained over a period for at least 5 days. The sulfenanilides **1b**-**c** also gave similar blue solutions by the same treatment to that described above. Typical visible (Fig. 1) and ESR (Fig. 2) spectra are illustrated, and the spectral data are listed in Table. As can be seen from the table, the ESR parameters of **2a**-**c** are close to that of **2e** and are distinct from that of the corresponding nitroxide radical **3**,[1] indicating that the present radicals are N-aryl-N-arylthioaminyls.

In order to confirm that the blue colors are attributable to the radicals **2**, the optical density at λmax (*e.g.* 602 nm in the case of **2a**) was plotted against the intensity of the ESR signal (Fig. 3). The good linearity of the plot indicates that the blue colors are attributable to **2**.

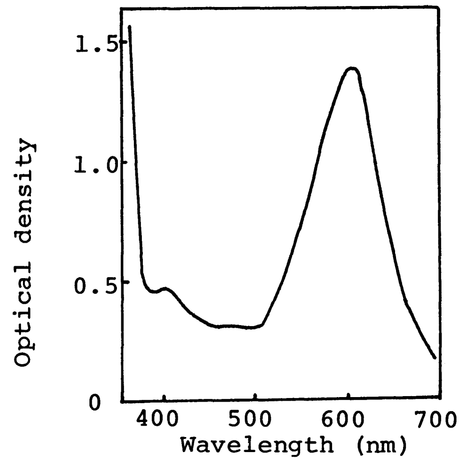


Fig. 1. The visible spectrum of **2a** in benzene.

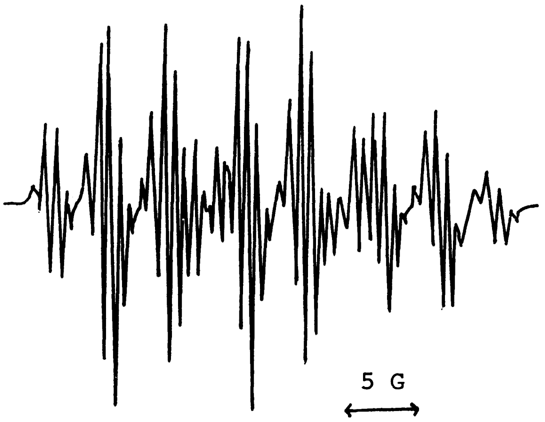


Fig. 2. The ESR spectrum of **2c** in benzene at room temperature.

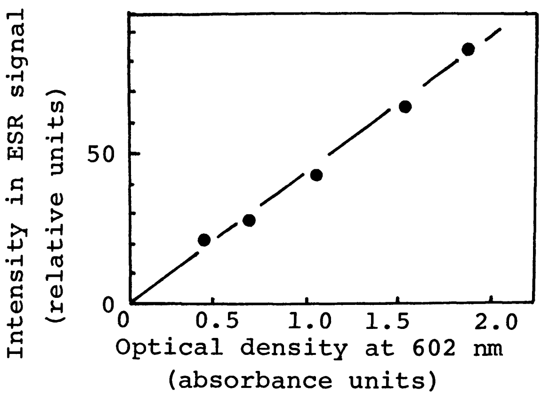


Fig. 3. Plot of ESR signal intensity *vs.* optical density (602 nm) for **2a** in benzene.

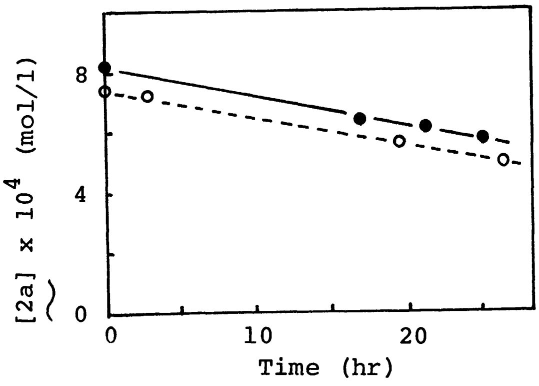
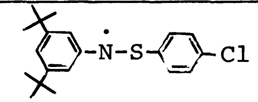
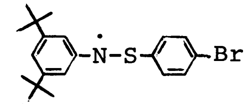
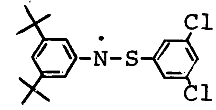
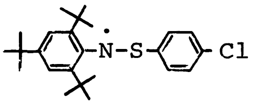
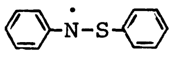
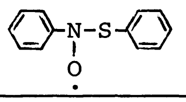


Fig. 4. Decay plot of **2a** in benzene at 23°C in the presence (——) and absence (- - -) of oxygen (the concentrations of **2a** were determined by means of ESR spectroscopic method)

Table. The ESR and visible spectral data for N-aryl-N-arylthioaminyls (2)$^{\text{a)}}$

Radical$^{\text{b)}}$			Coupling constant (G)						g-Value	λmax
			N-Phenyl ring			S-Phenyl ring				
		a_N	$a_{o\text{-}H}$	$a_{m\text{-}H}$	$a_{p\text{-}H}$	$a_{o\text{-}H}$	$a_{m\text{-}H}$	$a_{p\text{-}H}$		(nm)
2a		9.58	3.70	-	4.42	0.75		-	2.0059	602
2b		9.56	3.71	-	4.38	0.77	0.22	-	2.0059	602
2c		9.63	3.87	-	4.52	0.74	-	0.74	2.0057	590
2d		12.27	-		-			-	2.0067	660
2e$^{\text{c)}}$		9.59	3.70	1.26	4.18	0.78	0.27	0.84	2.0059	
3$^{\text{c)}}$		11.52	2.56	0.86	2.56					

a) In benzene at room temperature. b) + : t-Butyl. c) Reference 1.

The kinetic investigations of 2a were performed both in the presence and absence of oxygen (Fig. 4). As can be seen from the figure, 2a is fairly persistent. Furthermore, it seems that the radical is not sensitive to oxygen though it is a typical nitrogen-centered free radical. The parent compound 1a was not oxidized to 2a by the atmospheric oxygen.

Another t-butyl substituted N-aryl-N-arylthioaminyl, 2',4',6'-tri-t-butylphenyl-4-chlorophenylthioaminyl (2d), was also attempted to prepare. Although the parent anilide, 2',4',6'-tri-t-butyl-4-chlorobenzenesulfenanilide (1d), could not be isolated, a green residue was obtained in the course of the preparation of 1d.$^{4)}$ A benzene solution of the green residue afforded a strong ESR signal which was split into a broad 1:1:1 triplet. If the paramagnetic species is a radical cation, a large coupling due to the α proton should be observed. Therefore, the species may be the radical 2d or a nitroxide radical. The ESR parameters reported for 2,4,6-tri-t-butylphenyl phenylthio nitroxide are 16.29 (a_N) and 0.85 G ($a_{m\text{-}H}$).$^{5)}$ Thus, the detected species may be 2d. The radical 2d persisted in hexane over a period for 2 days, but it decayed in benzene within a few hours.

The value of a_N of **2d** is larger by ca. 2.7 G compared to the other radicals, **2a-c** and **2e**. In the case of **2d**, the N-phenyl ring may be twisted from the π system containing the unpaired electron by the steric effect of the two t-butyl groups at the ortho positions. Thus, the extent of delocalization of the unpaired electron into the N-phenyl ring is decreased, leading to an increase in the magnitude of a_N.

References and Notes

1) Part IV of this series, "ESR Studies of Nitrogen-centered Free Radicals." For Part III, see Y.Miura and M.Kinoshita, Bull.Chem.Soc.Jpn., in press.

2) C.M.Mikulski, P.J.Russo, M.S.Saran, A.G.MacDaiamid, A.F.Garito, and A.J.Heeger, J.Am.Chem.Soc., 97, 6358 (1975).

3) R.L.Greene, G.B.Street, and L.J.Suter, Phys.Rev.Lett., 34, 577 (1975).

4) The compound 1d has been attempted to prepare by the reaction of 2,4,6-tri-t-butylaniline with an equiv. of 4-chlorobenzenesulfenyl chloride in dry ether in the presence of triethylamine.

5) S.Terabe and R.Konaka, J.Chem.Soc., Perkin Trans. II, 1973, 369.

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