February, 1985] © *1985 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 58, 751—752 (1985)* 751

Triphenylmethyl-substituted Arylthioaminyl Radicals. An ESR Study of *N*-(Arylthio)triphenylmethylaminyls[1)]

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

(Received August 1, 1984)

Synopsis. The title radicals have been studied by ESR spectroscopy. The radicals are fairly long-lived in solution and satellite lines due to the ^{33}S atom at natural abundance could be observed in their ESR spectra.

Since the triphenylmethyl group is one of the most bulky groups, triphenylmethyl-substituted free radicals are expected to be sterically protected from reactions by which the free radicals will be destroyed.[2)] Therefore, this steric protection may make the free radicals more long-lived. From this viewpoint triphenylmethyl-substituted arylthioaminyls, **2**, are of considerable interest and the present work was initiated with the hope of isolating them. Thioaminyl radicals ($R\dot{N}SR'$) are essentially long-lived in solution,[3)] but the thioaminyl radicals stable enough to be isolated as the free radical substance are rare.[4)] The results of an ESR study of **2**, however, showed that **2** were not as stable as we had expected. Interestingly, however, in their ESR spectra satellite lines due to the ^{33}S atom at natural abundance could be observed for any **2** radical. Herein we report the $a_{^{33}S}$ values for **2** and discuss their electronic structures and plausible conformations on the basis of their ESR parameters.

$Ph_3CNHSAr$	$Ph_3C\dot{N}SAr$	$t\text{-}Bu\dot{N}SAr$
1	**2**	**3**

Radicals **2** were generated in benzene from **1** by either of the two methods described in the Experimental section. A typical ESR spectrum is illustrated in Fig. 1 and the ESR parameters are listed in Table 1. The ESR spectra obtained were very clean and the signals due to impurity radicals were either very weak or absent. These clean ESR spectra are in contrast to those of *N*-(arylthio)-*t*-butylaminyl radicals (**3**)[5)] in which an impurity radical, $t\text{-}Bu\dot{N}OBu\text{-}t$, was simultaneously recorded with comparable intensity.[6)] This difference may be explained in terms of the steric protection by the bulky triphenylmethyl group from the reactions by which impurity radicals will be produced.

Radicals **2** were fairly long-lived in solution. For instance, the steady-state radical concentrations obtained by method **a** were ≈10^{-4} mol dm^{-3}, and on interruption of UV-irradiation, the radicals persisted for a long period (≈10 h at room temperature), although they were not stable enough to be isolated.

As can be seen from Fig. 1, the ESR spectra of **2** showed relatively narrow lines and gave well resolved splittings due to the phenylthio aromatic protons. This contrasts with the broad and poorly resolved ESR spectra of **3**.[5)] Interestingly, this line narrowing permitted us clearly to observe the satellite lines due to the ^{33}S atom at natural abundance for any **2** radical, on recording at high gain. The measured intensities heights of the satellite lines correspond to ≈0.12% of the parent peak (theoretical 0.19%). The results are listed in Table 1.

The large a_N and large $a_{^{33}S}$ values for **2** strongly suggest that in **2** the unpaired electron resides mainly

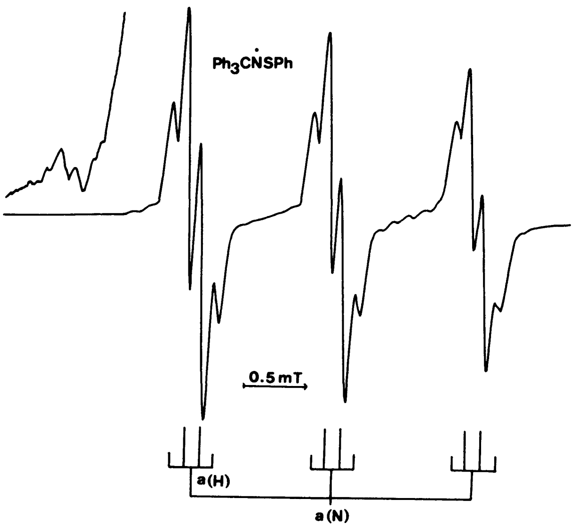

Fig. 1. ESR spectrum of **2a** recorded during photolysis of a solution of **1a** in 1:9 (v/v) di-*t*-butyl peroxide-benzene at 20 °C. The left wing is shown under high amplification (100 times) and the satellite lines due to the ^{33}S atom can be clearly seen.

TABLE 1. ESR PARAMETERS FOR *N*-(ARYLTHIO)-AND *N*-(*t*-BUTYLTHIO) TRIPHENYLMETHYLAMINYL RADICALS[a–c)]

$Ph_3C\dot{N}SR$	R	a_N	a_H[d)]	$a_{^{33}S}$	*g*
2a	Ph	1.171	0.119 (3)[e)]	0.683	2.0071
2b	$4\text{-}ClC_6H_4$	1.181	0.116 (2)[f)]	0.678	2.0071
2c	$3,5\text{-}Cl_2C_6H_3$	1.188	0.112 (3)[e)]	0.641	2.0068
2d[g)]	$2,4,6\text{-}Me_3C_6H_2$	1.209		0.740	2.0077
4	*t*-Bu	1.228			2.0076

a) Unless otherwise noted, the radicals are generated by method a (see, Experimental section). b) ESR measurements are carried out at 20 °C. c) Hyperfine splitting constants are given in mT. d) Numbers in parentheses refer to the number of equivalent protons. e) One para and two ortho protons of the phenylthio benzene ring. f) Two ortho protons of the phenylthio benzene ring. g) The radical is generated by method **b** (see, Experimenatl section).

on the nitrogen and sulfur. Furthermore, their ESR parameters (except those for **2d**) are similar to those for **3** (a_N=1.170—1.189 mT, g=2.0068—2.0072).[5] Therefore, it is likely that **2** adopt a similar conformation to that of **3** which we believe to be planar.[3]

To discuss the spin density distribution in **2** in more detail, the spin density on each atom was calculated by both the standard Hückel MO method and the McLachlan perturbation treatment,[7] assuming the radicals to be planar. The parameters used are as follows: $\alpha_N=\alpha+0.6\beta$, $\alpha_S=\alpha+\beta$, $\beta_{NS}=0.7\beta$, $\beta_{CS}=0.7\beta$, $\lambda=0.7$.[3] The spin densities on the nitrogen, sulfur and ortho and para carbons of the phenylthio benzene ring calculated by the Hückel MO method are 0.554, 0.325, 0.04, and 0.04, respectively.[8] Then, the a_N, a_{33}S, and a_H values derived from these values by use of the simple McConnell relationship $a_x=Q_x\rho_x{}^\pi$, where Q_N=2.2, Q_{33S}=2.3, and Q_H=−2.7 mT,[3] become 1.22, 0.75, and 0.11 mT, respectively. It is seen from Table 1 that these values are in good agreement with the experimental ones.

The ESR parameters (a_N, a_{33S}, and g) for **2d** are unusually increased compared with those for the other radicals. We believed that these unusual increases in the ESR parameters could be accounted for by assuming that **2d** adopted a twisted conformation in which the phenylthio benzene ring did not lie in the nodal plane of the nitrogen $2p_z$ (and sulfur $3p_z$) orbital. In this assumed conformation the unpaired electron will be poorly delocalized over the phenylthio benzene ring.[9] To confirm this assumption, *N*-(*t*-butylthio)triphenylmethylaminyl radical (**4**) was generated. If this assumption is correct, the ESR parameters for **2d** should come close to those for **4**. As can be seen from Table 1, the parameters for both radicals are very similar to each other. Consequently, it is concluded that the unusual increases in the ESR parameters for **2d** are attributable to the twisted conformation of **2d**.

Experimental

IR and ^{1}H NMR measurements have been described in a previous paper.[3] Di-*t*-butyl diperoxyoxalate,[10] triphenylmethylamine,[13] and alkane- and benzenesulfenyl chlorides[3,11,12] were prepared by the previously reported methods.

General Procedure for Preparation of N-*(Arylthio)triphenylmethylamines (1).* A benzenesulfenyl chloride (7.60 mmol) in 30 cm^3 of dry diethyl ether (ether) was added to a stirred solution of triphenylmethylamine (5.78 mmol) and triethylamine (3 cm^3) in dry ether (150 cm^3) at 0 °C. After being stirred for 1 h at 0 °C and for an additional 4 h at room temperature, the reaction mixture was filtered, evaporated, and the residue chromatographed on alumina (Merck art 1097, colum size 4×11 cm). Elution with hexane gave the diaryl disulfide and subsequent elution with 1:3 (v/v) benzene–hexane gave product **1** which was recrystallized from the appropriate solvent.

N-*(Phenylthio)triphenylmethylamine (1a).* Colorless prisms (from hexane); mp 116—118 °C; yield 67%; IR (KBr) 3300 cm^{-1} (NH); NMR (CDCl$_3$) δ=4.29 (s, 1H, NH, exchanged by D$_2$O) and 6.93—7.37 (m, 20H, aromatic). Anal. (C$_{25}$H$_{21}$NS) C, H, N.

N-*(4-Chlorophenylthio)triphenylmethylamine (1b).* Colorless prisms (from hexane–benzene); mp 151—153 °C; yield 46%; IR (KBr) 3280 cm^{-1} (NH); NMR (CDCl$_3$) δ=4.37 (s, 1H, NH, exchanged by D$_2$O) and 7.04—7.38 (m, 19H, aromatic). Anal. (C$_{25}$H$_{20}$ClNS) C, H, N.

N-*(3,5-Dichlorophenylthio)triphenylmethylamine (1c).* Colorless prisms (from hexane); mp 120—122 °C; yield 67%; IR (KBr) 3320 cm^{-1} (NH); NMR (CDCl$_3$) δ=4.38 (s, 1H, NH, exchanged by D$_2$O) and 6.87—7.34 (m, 18H, aromatic). Anal. (C$_{25}$H$_{19}$Cl$_2$NS) C, H, N.

N-*(2,4,6-Trimethylphenylthio)triphenylmethylamine (1d).* Colorless needles (from ethanol–benzene); mp 144—145 °C; yield 36%; IR (KBr) 3280 cm^{-1} (NH); NMR (CDCl$_3$) δ=2.21 (s, 6H, *o*-CH$_3$), 2.23 (s, 3H, *p*-CH$_3$), 3.85 (s, 1H, NH, exchanged by D$_2$O), and 6.78—7.35 (m, 17H, aromatic). Anal. (C$_{28}$H$_{27}$NS) C, H, N.

Although an attempt was made to prepare *N*-(*t*-butylthio)triphenylmethylamine (**1e**) by the reaction of triphenylmethylamine with 2-methyl-2-propanesulfenyl chloride, it could not be isolated from the reaction mixture. For ESR measurements the concentrate of the reaction mixture was used.

ESR Measurements. Radicals **2** were produced by either of the following two methods: (a) photolysis of a solution of **1** (20 mg) in 1:9 (v/v) di-*t*-butyl peroxide—benzene (0.4 cm^3) with a high-pressure mercury lamp and (b) reaction of **1** (25 mg) with di-*t*-butyl diperoxyoxalate (8 mg) in benzene (0.4 cm^3).

ESR spectra were recorded with a JEOL JES-ME-3X spectrometer. Hyperfine splitting constants and g values were determined by comparison with those (a_N=1.309 mT, g=2.0057) for Fremy's salt in K$_2$CO$_3$ aqueous solution.

References

1) Part 23 in the series "ESR Studies of Nitrogen-Centered Free Radicals." For part 22, see: Y. Miura, A. Yamamoto, and M. Kinoshita, *Electrochim. Acta*, **29**, 1731 (1984).

2) M. Kamachi, Y. Kuwae, S. Nosakura, K. Hatada, and H. Yuki, *Polymer J.*, **13**, 919, (1981).

3) Y. Miura, H. Asada, M. Kinoshita, and K. Ohta, *J. Phys. Chem.*, **87**, 3450 (1983).

4) Y. Miura, A. Yamamoto, Y. Katsura, M. Kinoshita, S. Sato, and C. Tamura, *J. Org. Chem.*, **47**, 2618 (1982).

5) Y. Miura, H. Asada, and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, **50**, 1855 (1977).

6) H. Woynar and K. U. Ingold, *J. Am. Chem. Soc.*, **102**, 3813 (1980).

7) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

8) The spin densities on the same atoms calculated by the McLachlan perturbation treatment are 0.754 (N), 0.234 (S), 0.023 (*o*-C), and 0.017 (*p*-C), which are in poor agreement with experiment.

9) Such a twisted conformation has also been assumed for polysubstituted arylthioaminyl radicals; Y. Miura, Y. Katsura, and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, **52**, 1121 (1979); Y. Miura and M. Kinoshita, *J. Org. Chem.*, **49**, 2724 (1984).

10) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960).

11) Y. Miura, N. Makita, and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, **50**, 482 (1977).

12) 2,4,6-Trimethylbenzenesulfenyl chloride was prepared by the reaction of 2,4,6-trimethylbenzenethiol with two equivalents of SO$_2$Cl$_2$ and used in the following step without distillation; J. Kuyper and G. B. Street, *J. Am. Chem. Soc.*, **99**, 7848 (1977).

13) C. A. Kraus and R. Rosen, *J. Am. Chem. Soc*, **47**, 2739 (1925).