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N,N'-BIS(ARYLTHIO)BENZAMIDINYL RADICALS. A NEW CLASS OF PERSISTENT NITROGEN-CENTERED FREE RADICALS[1]

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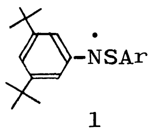
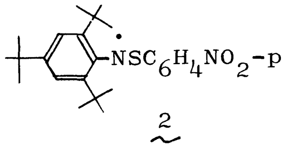
N,N'-Bis(arylthio)benzamidinyl radicals were generated and studied by ESR spectroscopy. They were extremely persistent in solution, even in the presence of oxygen.

Radical persistence is a function of electronic stabilization and steric protection. As for the electronic stabilization, it is well-known that radicals bearing atom(s) with the lone pair of electrons at the α position are strikingly stabilized by the conjugative electron delocalization with the lone pair of electrons. Typical examples are hydrazyl and nitroxide radicals.[2] On the basis of this concept, we have studied a variety of N-thioaminyl radicals ($R_1\dot{N}SR_2$) to obtain persistent radicals. In fact, we have found that N-thioaminyl radicals become extremely persistent, provided that reaction sites are protected by bulky gropus such as t-butyl.[3] For instance, radicals 1 and 2 can be isolated as dimer or radical crystals.[4,5] We have recently found that N,N'-bis(arylthio)benzamidinyl radicals (5), a new class of nitrogen-centered free radicals, persist over a long period with only a slight decomposition. As their structures show, the radicals are not sterically protected. Thus, they gain the persistence only by the electronic stabilization. In this letter we report the generation and ESR study of this new family of persistent nitrogen-centered free radicals.

X=N-R, O, S



1



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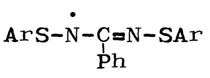
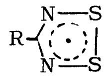


$ArS-\dot{N}-\underset{Ph}{C}=N-SAr$

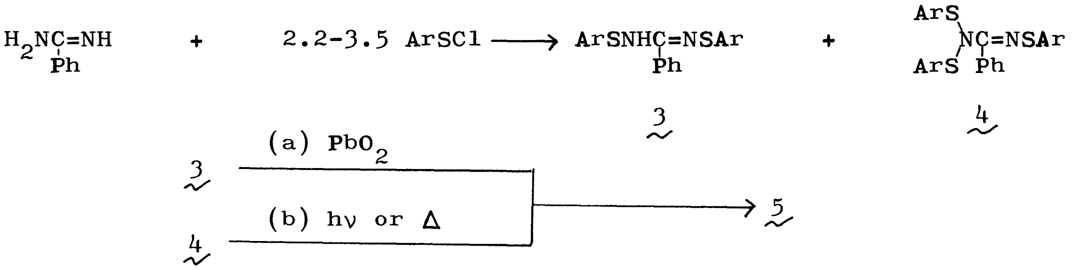
5



6 (R=CCl_3, Ph)

Radicals 5 were generated by two methods: (a) oxidation of N,N'-bis(arylthio)-benzamidines (3) with PbO_2; (b) photolysis of N,N,N'-tris(arylthio)benzamidines (4). In addition, they could also be generated by thermolysis of 4. The precursors were prepared by the reaction of benzamidine with 2.2-3.5 equiv arenesulfenyl chlorides. When p-chloro-, p-bromo-, and 3,5-dichlorobenzenesulfenyl chlorides were employed in the reaction, both 3 and 4 were obtained in 26-36 and

65-86% yields, respectively. However, the reaction with 3,5-dichlorobenzenesulfenyl chloride afforded only 3 in 52% yield and the reactions with benzene- and p-toluenesulfenyl chlorides yielded only 4 in 69-73% yields. Thus, radicals 5d-f could be generated by both methods mentioned above, but radicals 5a-c and 5g either by method a or b (see Table 1).



a: Ar=C_6H_5
b: Ar=C_6D_5
c: Ar=4-$CH_3C_6H_4$
d: Ar=4-ClC_6H_4
e: Ar=4-BrC_6H_4
f: Ar=2,4-$Cl_2C_6H_3$
g: Ar=3,5-$Cl_2C_6H_3$

A representative ESR spectrum is illustrated in Fig. 1. As can be seen from the figure, the ESR signal is constituted of a simple 1:2:3:2:1 quintet with a relatively large line-width. Almost identical ESR spectra were also found for 5c-f. However, in the spectrum of 5g, the quintet lines were further split by the interaction with the S-aromatic protons, though the resolution was very poor. In addition, in the spectrum of 5b, ^{33}S hyperfine splittings (hfs's) could be detected in the wings of the spectrum, without any enrichment of ^{33}S atoms, when a concentrated solution of 5b was used.[6] The ESR parameters for 5 are summarized in Table 1. As can be seen from Fig. 1, two nitrogens in 5 are magnetically equivalent and the hfs constants are in the range 0.603-0.626 mT. Similarly, two sulfurs are also magnetically equivalent and its hfs constant is 0.331 mT (for 5b).

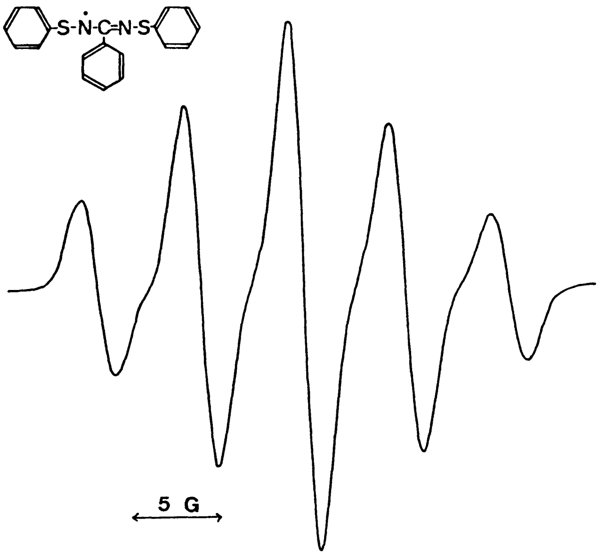


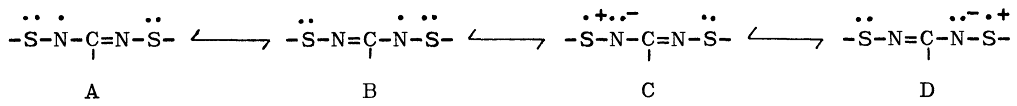
Fig. 1. ESR spectrum of 5a in benzene at 16°C.

Table 1. ESR parameters for 5[a]

	Method[b]	a_N/mT	a_{other}/mT	g
5a	b	0.609		2.0074
5b	b	0.608	0.331(^{33}S)	2.0074
5c	b	0.603		2.0074
5d	a	0.613		2.0074
	b	0.612		2.0074
5e	a	0.609		2.0078
	b	0.607		2.0078
5f	a	0.610		2.0073
	b	0.610		2.0073
5g	a	0.626	0.053[c]	2.0070

[a] In benzene at 16°C. [b] Method of generation of radicals; see: Text. [c] Due to S-aromatic protons.

On the other hand, the splitting due to the S-aromatic protons is only 0.053 mT, and those attributable to the C-aromatic protons were never found. On the basis of these results of ESR spectroscopy, we can safely conclude that in 5 the unpaired electron resides mainly on two nitrogens and sulfurs. This is also supported by the Hückel molecular orbital calculations.7) Thus, radicals 5 can be represented by four principal resonance structures A-D. When the S-benzene rings bear an electron-withdrawing substituent, resonance structures A and B will be reinforced, leading to an increase in the magnitude of a_N. On the contrary, when they bear an electron-donating substituent, resonance structures C and D will be reinforced, leading to a reduction in the magnitude of a_N. The highest a_N value for 5g and the lowest a_N value for 5c can be rationalized by this effect. Furthermore, the relatively large g values of 5 for nitrogen-centered radicals can be interpreted in terms of the considerable delocalization of the unpaired electron onto the sulfurs.8,9)



$$-\overset{\bullet\bullet}{\text{S}}-\overset{\bullet}{\text{N}}-\underset{|}{\text{C}}=\overset{\bullet\bullet}{\text{N}}-\text{S}- \longleftrightarrow -\overset{\bullet\bullet}{\text{S}}-\text{N}=\underset{|}{\text{C}}-\overset{\bullet}{\text{N}}-\overset{\bullet\bullet}{\text{S}}- \longleftrightarrow -\overset{\bullet+\bullet}{\text{S}}-\overset{\cdot-}{\text{N}}-\underset{|}{\text{C}}=\overset{\bullet\bullet}{\text{N}}-\text{S}- \longleftrightarrow -\overset{\bullet\bullet}{\text{S}}-\text{N}=\underset{|}{\text{C}}-\overset{\bullet\bullet-}{\text{N}}-\overset{\bullet+}{\text{S}}-$$

A B C D

Radicals 5 are structurally very close to the cyclic thioaminyl radicals, 6, which were recently reported by Markovski et al.,10) we can regard 5 as the linear analogue of 6. The reported a_N and g values are 0.49 mT and 2.0104, respectively. Thus, the a_N value for 6 is 0.11-0.14 mT lower than those for 5. This reduction in the magitude of a_N and the larger g value of 6 suggest that the extent of delocalization of the unpaired electron onto sulfurs is greater in 6 than in 5.

Radicals 5 are quite persistent, even in the presence of oxygen. When being treated with PbO$_2$, colorless benzene solutions of 3 immediately turned dark green (5d-f) or brown (5g), and the resulting solutions retained its color over a long period under atmosphere. In order to examine the stability of 5 in more detail, the radical concentration was followed as a function of time. The results are shown in Fig. 2. The radical solution was obtained by treating 3g with PbO$_2$ under atmosphere and the ESR cell used was not sealed (the solution was always contacted with air). As can be seen from the figure, radical 5g persisted over a long period with only a slight decomposition, even in the presence of oxygen. Similar results were also obtained for other 5. The oxidation of 3 with PbO$_2$ was found, from TLC inspection, to proceed in relatively in good yields, particularly for 3f and 3g, and removal of the benzene from the radical solutions through freeze-drying left a green powder. Upon dissolution of this powder, the resulting solution showed a green or brown color and gave a strong

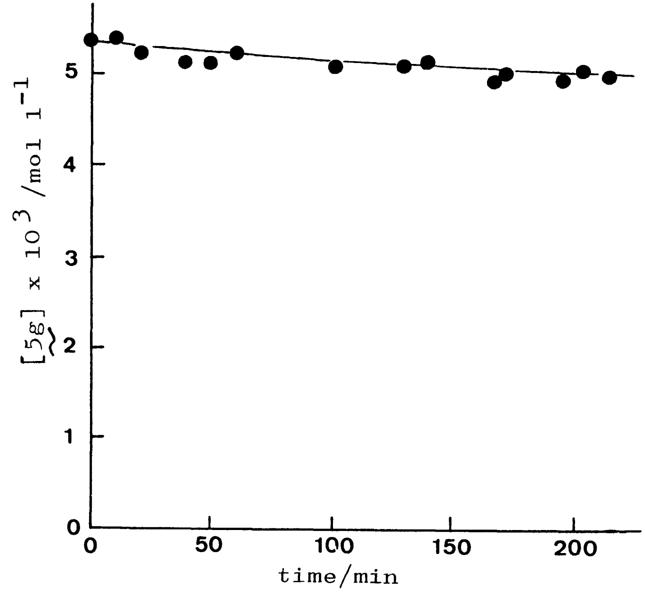


Fig. 2. Decay plots of 5g in benzene at 14°C in the presence of air (ESR cell was not sealed).

ESR signal due to 5. We consider this powder is a dimer of 5,[11] but it contains significant amounts of impurities. Further experiment is in progress.

References

1) Part 20 in the series "ESR Studies of Nitrogen-Centered Free Radicals." For part 19, see: Y. Miura, H. Asada, M. Kinoshita, and K. Ohta, J. Phys. Chem., in press.

2) A. R. Forrester, J. M. Hay, and R. H. Tomson, "Organic Chemistry of Stable Free Radicals," Academic Press, London (1968).

3) Unless 1 and 2 are protected by t-butyl groups, they will become very short-lived. For instance, $\mathrm{Ph\dot{N}SPh}$ radical is rather transient, see: Y. Miura and M. Kinoshita, Bull. Chem. Soc. Jpn., 50, 1142 (1977); H. Sayo, K. Mori, T. Michida, Chem. Pharm. Bull., 27, 351 (1979).

4) Y. Miura, A. Yamamoto, Y. Katsura, and M. Kinoshita, J. Org. Chem., 45, 3875 (1980).

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

6) In other spectra, satellites due to ^{33}S could not be detected because of the broad lines.

7) Unpublished results.

8) The g values of ordinary aliphatic and aromatic nitrogen-centered free radicals are in the range 2.003-2.004, see: W. C. Danen and F. A. Neugebauer, Angew. Chem., Int. Ed. Engel., 14, 783 (1975). See also ref. 2.

9) The spin-orbit coupling parameter for sulfur is 382 cm^{-1}, see: D. S. McClure, J. Chem. Phys., 17, 905 (1949).

10) L. N. Markovski, O. M. Polumbrik, V. S. Talanov, and Y. G. Shermolovich, Tetrahedron Lett. 23, 761 (1982).

11) The assumption that radicals 5 are in equilibrium with its dimer in solution comes from the following finding; when hexane solutions of 5 were cooled to -78°C, the characteristic green or brown colors of 5 disappeared or became light and, on raising to room temperature, the colors reappeared again or became deep and this cycle was completely reversible.

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