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AN ELECTRON SPIN RESONANCE STUDY OF A NEW TYPE STABLE FREE NITROGEN-CENTERED RADICAL, DIBENZENESULFENAMIDYL RADICALS

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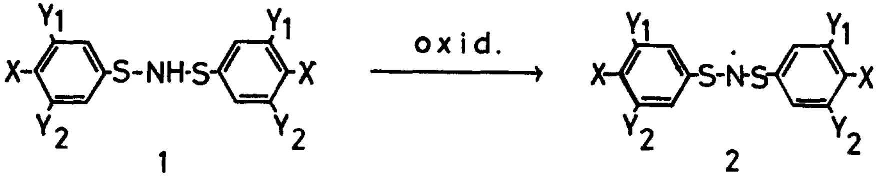
A benzene solution of dibenzenesulfenamide (1a) turns purple immediately on the oxidation with lead dioxide, as shown in Lecher's report.$^{1)}$ We have now carried out an electron spin resonance (e.s.r.)study of the system, and found that a stable free nitrogen-centered radical, dibenzenesulfenamidyl radical (2a) , is formed in this system. The radical is of interest, for it is a new type nitrogen-centered radical in which two sulfur atoms are present at the α position, and has a life of a week in non-polar solvents such as benzene and n-hexane.

In the present report an e.s.r. study of 2a and its related radicals (2b-2g) is described.



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1a, 2a : $X=Y_1=Y_2=H$
1b, 2b : $X=CH_3$, $Y_1=Y_2=H$
1c, 2c : $X=NO_2$, $Y_1=Y_2=H$
1d, 2d : $X=Cl$, $Y_1=Y_2=H$
1e, 2e : $X=Br$, $Y_1=Y_2=H$
1f, 2f : $X=Y_1=H$, $Y_2=Cl$
1g, 2g : $X=H$, $Y_1=Y_2=Cl$

In a typical treatment, 1 (0.01 g) was treated with lead dioxide (0.5 g) in 1 ml of benzene in the presence of potassium carbonate (0.5 g), and after the inorganic compounds were removed, the benzene solution was degassed by three freeze-thaw cycles, and an e.s.r. measurement was carried out at ambient temperature. The spectra observed are shown in Figure 1-4.

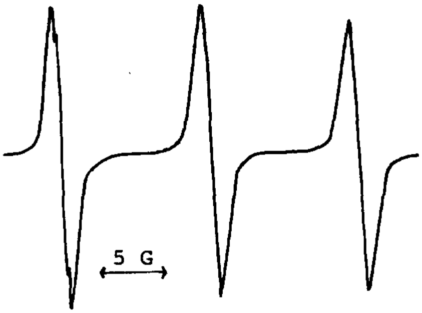

Figure 1. The e.s.r. spectrum of 2a in benzene

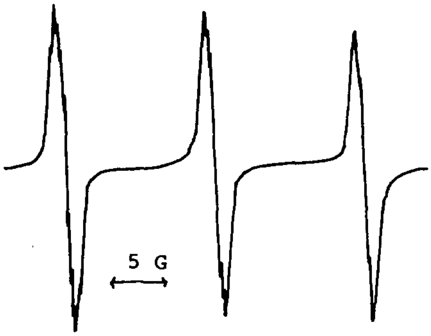

Figure 2. The e.s.r. spectrum of 2e in benzene

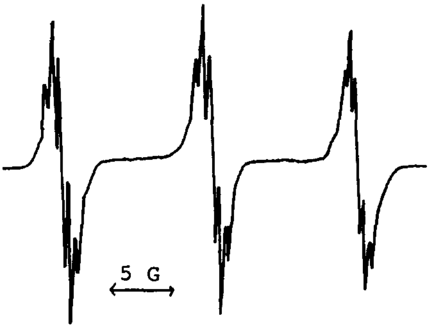

Figure 3. The e.s.r. spectrum of 2f in benzene

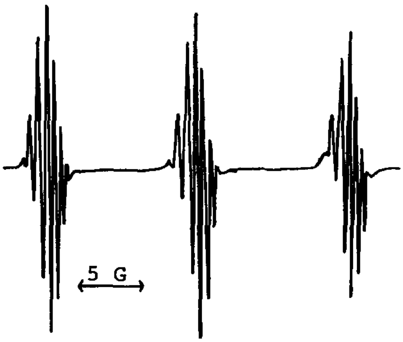

Figure 4. The e.s.r. spectrum of 2g in benzene

The spectrum of 2a consists of a simple 1:1:1 triplet, couplings due to the ring protons could not be observed. The similar spectra were also observed for 2b and 2c. In the spectra of 2d-2g (Figure 2-4), however, the couplings due to the ring protons could be further observed in addition to those due to the nitrogen nuclei, and in the case of 2g a particularly well-resolved spectrum was obtained (Figure 4). The coupling constants are summarized in Table, together with g-values.

The same radicals could be also formed by the hydrogen-abstraction of 1 by 2-cyano-2-propyl or tert-butoxy radicals, for example, a degassed benzene solution (1 ml) of 1a (0.01 g) and di-tert-butyl peroxide (0.1 ml) was irradiated with a high pressure mercury-lamp to turn purple immediately, and the e.s.r. spectrum of the solution indicated that 2a was formed in the system (a_N =11.41 G, g=2.0082), thus a possibility that 2a-2g were stable nitroxide radicals was thoroughly excluded.

All these radicals show, as mentioned above, the characteristic absorptions in the 497-545 nm region corresponding to the purple color (Figure 5), the absorption maxima are also given in the Table.

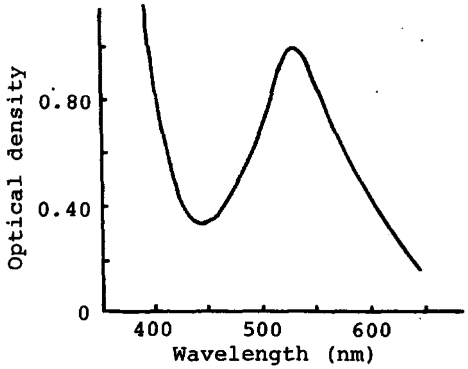

Figure 5. The visible spectrum of 2a in benzene

Table

The e.s.r. parameters of the dibenzenesulfenamidyl radicals 2 (in benzene)

	a_N in G	a_{o-H} in G	a_{m-H} in G	a_{p-H} in G	g	λmax in nm
2a	11.41				2.0082	538
2b	11.45			-	2.0082	545
2c	11.26			-	2.0080	497
2d	11.37	o.56		-	2.0082	543
2e	11.37	0.56	0.28	-	2.0083	544
2f	11.40	0.57		0.57	2.0081	535
2g	11.40	0.58	-	0.58	2.0080	531

As found in the Table the nitrogen coupling constants lie in the range of 11.26 to 11.45 G, while the proton coupling constants are very small, indicating that most of the unpaired-electron localize on the nitrogen and two sulfur atoms, therefore, the spin density on the rings is significantly small. The g-values of these radicals are unusually large for a nitrogen-centered radical,[2)] these large values can be explained in terms of the large spin density on the sulfur atoms.[3)]

These radicals are not sensitive to oxygen, and are fairly stable in non-polar solvents such as benzene and n-hexane; all radicals except for 2c have a life of at least more than a few days, while 2c is less stable and decomposed thoroughly in a few days.

A kinetic study of decay of the radicals is under investigation.

REFERENCES

1) H. Lecher, K. Koberle, and P. Stöcklin, Chem. Ber., 58, 423 (1925).

2) e.g., 1,1-diphenyl-2-picrylhydrazyl : 2.0036, R. G. Bennett and A. Henglein, J. Chem. Phys., 30, 1117 (1957); diphenylamino radical : 2.0032, F. A. Neugebauer and S. Bamberger, Chem. Ber., 107, 2362 (1974); 1,3,5-triphenylverdazyl : 2.0033, R. Kuhn and H. Trischmann, Monatsh. Chem., 95, 457 (1964).

3) The spin-orbit coupling parameter of sulfur is 382 cm^{-1}, which is very larger than those of carbon, nitrogen, and oxygen.
D. S. McClure, J. Chem. Phys., 20, 682 (1952).