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An Electron Spin Resonance Study of the Anion Radicals of 2,1,3-Benzoselenadiazole and Related Compounds

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In the course of several recent ESR studies[1,2] of the aromatic anion radicals containing selenadiazole- or thiadiazole-ring little has been established about the effects of the preparation conditions on the spin distribution or about the electronic situation of the selenium atom. In the present work the titled anion radicals have been prepared first by metal reductions in several solvents at low temperatures. The solvent effect on the nitrogen hyperfine splitting constants is discussed in terms of a meso-ionic structure associated with the present compounds. Also, a few remarks are given about the possibilities of *p*- and *d*-orbital models for the selenium atom using information about the experimental hydrogen hyperfine splitting constants.

Experimental

The ESR measurements were done with a JES-3BS-X-type spectrometer with 100 kc/sec field modulation at −60—+20°C. The line separations were checked by referring to the spectra of an aqueous solution of peroxylamine disulfonate. The *g*-values were determined with a sample marker of Mn^{2+} in MgO. The anion radicals were prepared by a standard technique of metal reduction. Solvents used (THF, DME, DMF, THP, and Me-THP) were all obtained from the Merck Co. and were carefully dried by the usual methods. The 2,1,3-benzothiadiazole[3] and -benzoselenadiazole[4] were synthesized by reactions of *o*-phenylenediamine with thionyl chloride and selenium dioxide respectively. The 2-methyl-2,1,3-benzotriazole was obtained by the reaction of benzotriazole with diazomethane.[5] The compounds were purified by repeated sublimations under a high vacuum.

Results and Discussion

The instabilities of the former two anion radicals are predicted by the active metalation reactions as has been reported previously.[6] In fact, the hyperfine spectra of benzothiadiazole and benzoselenadiazole anion radicals could be observed only below a temperature of −40°C; at room temperature the sample solutions allowed to come in contact with a metal mirror readily yielded intensely-coloured solutions (purple in the former

1) G. A. Russell, E. G. Janzen and E. T. Strom, *J. Amer. Chem. Soc.*, **86**, 1807 (1964).

2) E. T. Strom and G. A. Russell, *ibid.*, **87**, 3326 (1965).

3) A. M. Khaletskii and V. G. Pesin, *Chem. Abstr.*, **46**, 106 (1952).

4) E. Sawicki and F. E. Ray, *J. Org. Chem.*, **19**, 1903 (1954).

5) N. O. Cappel and W. C. Fernelius, *ibid.*, **5**, 40 (1940).

6) M. Ziegler and O. Glemser, *Chem. Ber.*, **91**, 2889 (1958).

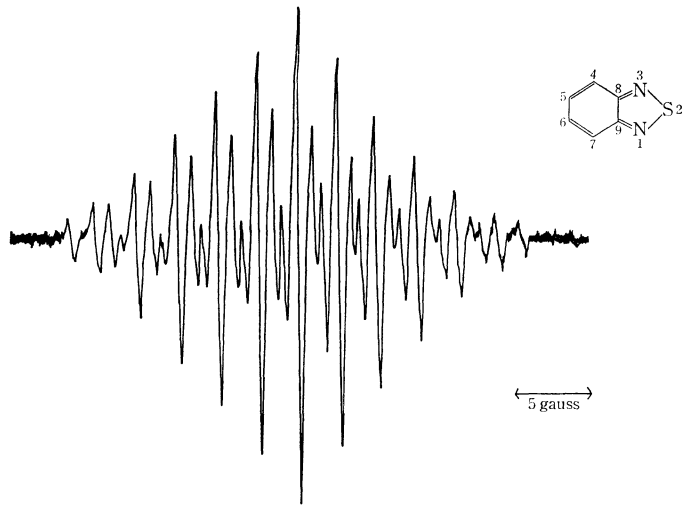


Fig. 1(a). The spectrum of 2,1,3-benzothiadiazole anion radical in THF at −40°C produced by potassium reduction.

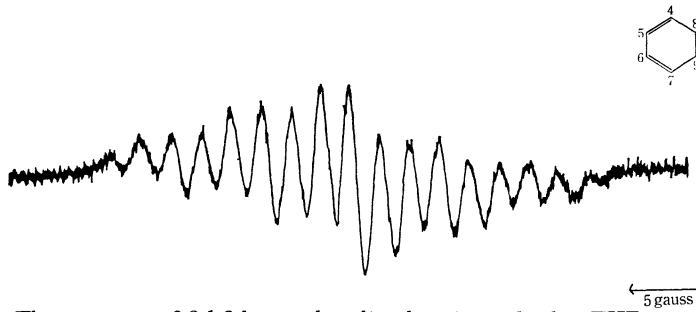


Fig. 1(b). The spectrum of 2,1,3-benzoselenadiazole anion radical in THF at −40°C produced by potassium reduction.

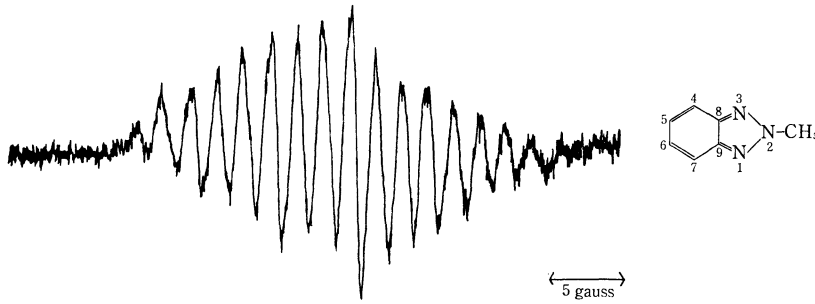


Fig. 1(c). The spectrum of 2-methyl-2,1,3-benzotriazole anion radical in THF at −40°C produced by potassium reduction.

and yellow in the latter) which showed rather asymmetric singlets with $g=2.004_0$—2.004_5 and $\Delta Hmsl=15$—20 gauss. This suggests the existence of more than one radical species although the existence of only one mono-negative radical species has been suggested from a study of the absorption spectrum of the metal-reduced benzoselenadiazole solution in THF.[7] 2,1,3-Benzoxadiazole produced no ESR signals in metal reduction; it simply showed a colour-change to dark green.

Some of the spectra are illustrated in Fig. 1, while the hyperfine splitting constants determined from the spectra are summarized in Table 1. The results indicate the noticiable facts that, as for benzothiadiazole and benzoselenadiazole, a decrease in a^N and a concurrent increase in the sum of a^H take place in the sequence of; DMF< THF≈DMF<THP≈Me-THP, although both a^N and a^H are not much affected by the cation species and no metal splittings are detected in any case.

7) J. Fajer, *J. Phys. Chem.*, **69**, 1773 (1965).

8) W. Baker, W. D. Ollis and V. D. Poole, *J. Chem. Soc.*, **1950**, 1546; E. S. Lane and C. Williams, *ibid.*, **1955**, 1468.

TABLE 1. THE HYPERFINE SPLITTING CONSTANTS (a^H AND a^N) OBTAINED IN METAL REDUCTIONS AT −40°C

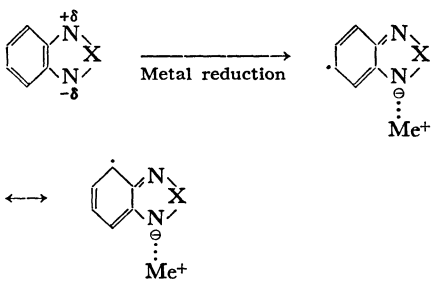
		DMF	DME	THF	THP	Me-THP
2,1,3-Benzothiadiazole	$a^N_{1,3}$	5.47	5.33	5.36(5.30)	5.09(5.05)	5.10
	$a^H_{4,7}$	2.59	2.65	2.68(2.72)	2.75(2.81)	2.75
	$a^H_{5,6}$	1.55	1.64	1.62(1.65)	1.68(1.65)	1.71
2,1,3-Benzoselenadiazole	$a^N_{1,3}$	5.72	5.67	5.64(5.64)	5.32(5.30)	5.35
	$a^H_{4,7}$	1.85	1.88	1.88(1.85)	1.95(1.92)	1.92
	$a^H_{5,6}$	1.85	1.88	1.88(1.85)	1.95(1.92)	1.92
2-Methyl-2,1,3-benzotriazole	$a^N_{1,3}$	5.40	5.22	5.25	5.28	5.30
	$a^H_{4,7}$	1.68	1.74	1.75	1.79	1.75
	$a^H_{5,6}$	1.68	1.74	1.75	1.79	1.75

An initial value of the h.f.s.c. (in gauss) shows the one (a mean value of several recordings) obtained in K-reduction and a value in parenthesis shows the one obtained in Na-reduction.

TABLE 2. SPIN DENSITIES IN ANION RADICAL AND ELECTRON DENSITIES IN NEUTRAL MOLECULE CALCULATED FOR 2,1,3-BENZOSELENADIAZOLE WITH A FEW OPTIMUM PARAMETERS ASSIGNED TO Se WITH A *p*-ORBITAL MODEL

			Se	$N_{1,3}$	$C_{4,7}$	$C_{5,6}$	$C_{8,9}$
$h^{\cdot\cdot}_{Se}=1.0$	$k_{NSe}=0.2$						
	HMO	q	1.915	1.188	1.002	0.959	0.894
	HMO	ρ	0.041	0.279	0.073	0.067	0.061
	McLachlan	ρ	0.041	0.322	0.054	0.054	0.049
$h^{\cdot\cdot}_{Se}=1.1$	$k_{NSe}=0.2$						
	HMO	q	1.928	1.185	1.002	0.957	0.892
	HMO	ρ	0.034	0.280	0.073	0.067	0.062
	McLachlan	ρ	0.035	0.324	0.054	0.054	0.050
$h^{\cdot\cdot}_{Se}=1.2$	$k_{NSe}=0.2$						
	HMO	q	1.939	1.183	1.001	0.956	0.890
	HMO	ρ	0.029	0.281	0.073	0.068	0.063
	McLachlan	ρ	0.030	0.325	0.054	0.055	0.051

Accordingly, it may be assumed that there exists a specific solvent effect giving rise to a decrease in the nitrogen spin density followed by an increase in the nitrogen electronegativity. A probable explanation of the current effect is that, because of the meso-ionic structure associated with these compounds, the above tendency is more promoted in a solvent with less ability at solvating cations according to the resonance structures of the anion radicals which enable a selective electrostatic interaction between the nitrogen and the metal cation as shown below.



The effects of temperatures on the hyperfine splitting constants appeared to be somewhat complex as a result of the variations in the line-width.

Meanwhile, we found that the spectrum of the benzoselenadiazole anion radical has a pattern very similar to that of 2-methyl-2,1,3-benzotriazole, as is illustrated in Fig. 1 (b) and (c). This indicates that the replacement of the selenium atom with the *N*-methyl group has little effect on the spin distribution. Hückel- and McLachlan-calculations of spin densities based upon a *p*-orbital model for the selenium atom yielded the values of $h^{\cdot\cdot}_{Se}=1.0$—1.1 and $k_{SeN}=0.2$—0.3 as the optimum parameters for reproducing an equal spin density of the four ring carbons. It should be noted here that these parameters do not reflect the solvent effect on the nitrogen hyperfine splitting constant since the equality of the four a^H values holds in various solvents. (In the McLachlan calculation the λ-value involved in a corrected Coulomb integral, $\alpha_r(\alpha_r=\alpha^\circ_r+2\lambda\rho^\circ_r\beta)$, was taken to be 1.2, while $h^{\cdot}_N$ and k_{CN} were fixed as the well-accepted values of $h^{\cdot}_N=0.5$ and $k_{CN}=1.0$.) The spin- and electron-densities calculated with the optimum parameters are given in Table 2.

By comparing the current results with those for benzothiadiazole,[2] we can conclude that the conjugation of the nitrogen atom with an adjacent carbon atom is greater in benzoselenadiazole; this conclusion indicates that, as has previously been mentioned, if a major contribution to the hybrid

structure contains a meso-ionic form with oppositely-charged nitrogens, this form should be more associated with benzoselenadiazole because the exchange of the nitrogen charges is essentially intermediated by the C–C conjugated bonds between the two nitrogens. This assumption is in harmony with the observed reactivities in mono-nitrogen quarternisation[9] (benzoselenadiazole>benzothiadiazole), which can be activated by the presence of negatively-charged nitrogen.

A *d*-orbital model accepted for the sulfur atom[2] was also tested; the optimum parameters were found to be $h_{Se}=0.1-02.$, $k_{NSe}=0.05-0.07$, and $k_{SeSe}'=1.0$. However, this model seems to be unreasonable, as has been indicated in dibenzoselenophene,[10] in part at least because of a too small k_{NSe} value as compared with k_{NS} (=0.8) in benzothiadiazole.[2]

9) A. J. Nunn and J. T. Raiph, *J. Chem. Soc.*, **1965**, 6769; *ibid.*, **1966**, 1568.

10) R. Gerdil and E. A. C. Lucken, *J. Amer. Chem. Soc.*, **87**, 213 (1965).