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An ESR Study of *N*,*N*-Bis(arylthio)aminyls. ^{33}S Hyperfine Splittings[1)]

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Synopsis. In the ESR spectra of *N*,*N*-bis(phenylthio)-, *N*,*N*-bis(phenyl-d_5-thio)-, and *N*,*N*-bis(3,5-dichlorophenylthio)aminyls, ^{33}S hyperfine splittings were detected. The spin densities in the aminyls were calculated by using the HMO calculations with and without McLachlan's correction, and the results were compared with the values derived from the ^{1}H, ^{14}N, and ^{33}S hyperfine splittings by use of the relationship $a=Q\rho$.

In a previous report on an ESR study of *N*,*N*-bis(arylthio)aminyls (**2**),[2,3)] it was shown from the ^{1}H and ^{14}N hyperfine splitting (hfs) constants that in **2** the spin resides mainly on the central nitrogen atom and the two adjacent sulfur atoms. In continuing this study, we have tried to detect satellites due to ^{33}S (I=3/2) in ESR signals of **2**. It is well known that

$$\underset{\mathbf{1}}{\text{Ar-S-NH-S-Ar}} \xrightarrow{-\text{H}\cdot} \underset{\mathbf{2}}{\text{Ar-S-}\dot{\text{N}}\text{-S-Ar}}$$

a: Ar=C_6H_5, **b**: Ar=C_6D_5, **c**: Ar=3,5-$Cl_2C_6H_3$

the detection of satellites due to ^{33}S in natural abundance is very difficult because of the small amount present (0.74%). Fortunately, we have been successful in the detection of the satellites due to ^{33}S in the spectra of **2** without an enrichment of ^{33}S atoms. From the ^{1}H, ^{14}N, and ^{33}S hfs constants for **2**, we derived the spin densities in **2** by use of the relationship $a=Q\rho$, and compared the values with those obtained from the HMO calculations with and without McLachlan's correction.[4)] In this report these results are described.

Results and Discussion

The aminyls **2** were generated by oxidation of *N*-(arylthio)arenesulfenamides (**1**) with lead dioxide and potassium carbonate.[2,5,6)] Since **2** are fairly persistent, we could easily obtain high concentration solutions of **2** by this procedure. A typical ESR spectrum of **2b** is illustrated in Fig. 1a. The signal is composed of a simple 1:1:1 triplet with a small line-width (0.035 mT). On recording under high amplification, the satellite due to ^{33}S in natural abundance was detected, together with the satellite due to ^{15}N (I=1/2) in natural abundance (0.37%). The ratio of the observed splittings of $a_{^{15}N}/a_{^{14}N}$ (1.40) agrees with that of the magnetic moments of the nuclei (1.40). In the spectrum of **2a**, the satellite due to ^{33}S was also detected, but it was significantly masked by the main spectrum because of the large line-width of the spectrum (0.16 mT). However, the obtained value was in good agreement with that for **2b**. In the spectrum of **2c**,

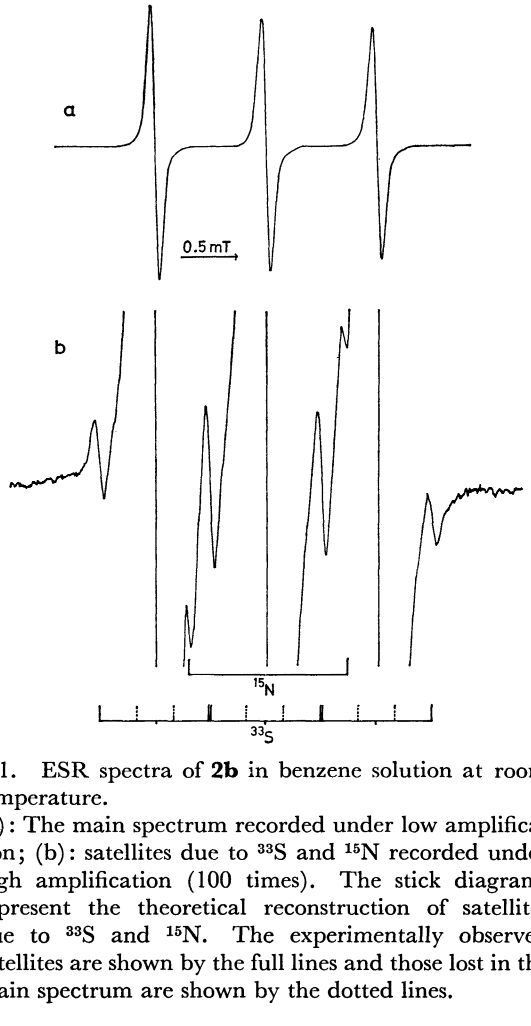


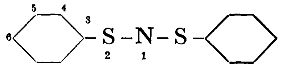
Fig. 1. ESR spectra of **2b** in benzene solution at room temperature.
(a): The main spectrum recorded under low amplification; (b): satellites due to ^{33}S and ^{15}N recorded under high amplification (100 times). The stick diagrams represent the theoretical reconstruction of satellites due to ^{33}S and ^{15}N. The experimentally observed satellites are shown by the full lines and those lost in the main spectrum are shown by the dotted lines.

Table 1. Hyperfine splitting constants and λ_{max} for **2**

	Solvent	$a_{^{14}N}$/mT	a_{other}/mT	*g*-value	λ_{max}/nm
2a	Benzene	1.141[a)]	0.39(^{33}S)	2.0075[b)]	538[a)]
2b	Benzene	1.144	0.39(^{33}S), 1.60 (^{15}N)	2.0075	538
2b	Hexane	1.151		2.0074	531
2b	THF	1.143		2.0075	534
2b	Acetone	1.141		2.0075	531
2b	Acetonitrile	1.140		2.0075	527
2c	Benzene	1.140[a)]	0.058 (*o*- and *p*-^{1}H),[a)] 0.39(^{33}S)	2.0073[b)]	531[a)]

a) See Ref. 2. b) See Ref. 7.

TABLE 2. OBSERVED AND CALCULATED SPIN DISTRIBUTION IN **2a**



Position	Observed hfs constant mT	Spin density	HMO	McLachlan
1	1.141(^{14}N)	0.496	0.503	0.688
2	0.39(^{33}S)	0.12	0.174	0.136
3	—		0.000	−0.014
4	0.058(^{1}H)[b]	0.021	0.025	0.018
5			0.000	−0.008
6	0.058(^{1}H)[b]	0.021	0.025	0.015

a) The spin densities (ρ) were derived from the hfs constants (a) using the relationship: $a=Q\rho$; $Q^{\pi}_{^{14}N}=2.3$ mT,[8c,d] $Q_{^{1}H}=-2.7$ mT,[10] $Q^{\pi}_{^{33}S}=3.3$ mT,[8b,11] $\lambda=0.7$. b) The value observed for **2c**.

the satellite due to ^{33}S was split into a septet, with an interval of 0.058 mT, by the interaction with the six magnetically equivalent protons. The ^{1}H, ^{14}N, ^{15}N, and ^{33}S hfs constants are listed in Table 1.

The ^{14}N hfs constant and the λ_{max} for **2b** were measured in some nonpolar and polar solvents in order to examine solvent effects on these values. As can be seen in Table 1, these values are independent of solvent. Thus, the spin distribution in **2** is little affected by the polarity of the solvent.

The HMO calculations with and without McLachlan's correction were made for **2a** using the following parameters:[8,9] $\alpha_N=\alpha+0.9\beta$, $\alpha_S=\alpha+1.3\beta$, $\beta_{NS}=0.7\beta$, $\beta_{CS}=0.75\beta$, $\lambda=0.7$; these parameters are chosen on the basis of the previously used values, but are slightly varied to give the best fit with the experimental results. In Table 2 the results are compared with the experimental values. Since, in the spectrum of **2a**, the splittings due to the ring protons were not detected, the values for **2c** are shown in Table 1. As can be seen from the comparison of the ^{14}N and ^{33}S hfs constants for **2a** with those for **2c**, the spin distributions in these aminyls are almost identical with each other. Thus, we can derive the spin densities on the phenyl rings of **2a** from the ^{1}H hfs constants for **2c**. As can be seen from Table 2, better agreement between the experimental and calculated values of the spin densities is obtained from the HMO calculation. The results indicate that in **2** *ca.* 50% of the spin resides on the central nitrogen atom and *ca.* 12% resides on each sulfur atom. The large *g*-values observed for **2** and other *N*,*N*-bis(arylthio)aminyls[2,7] (2.0073—2.0076) are well explained by this considerable delocalization of the spin onto the adjacent sulfur atoms, which have a large spin-orbit coupling parameter (382 cm^{-1}).[12,13]

Experimental

The visible spectra were obtained with a Hitachi Model ESP-3T spectrometer. The ESR spectra were obtained with a JES-ME-3X spectrometer equipped with an X-band microwave unit and 100 kHz field modulation. The hfs constants and *g*-values were determined in comparison with the ^{14}N hfs constant (1.309 mT) and the *g*-value (2.0055) of Fremy's salt. *N*-(Phenylthio)benzenesulfenamide (**1a**) and *N*-(3,5-dichlorophenylthio)-3,5-dichlorobenzenesulfenamide (**1c**) were prepared by the reported method.[2]

*N-(Phenyl-*d$_5$*-thio)benzene-*d$_5$*-sulfenamide (**1b**).* The amide was prepared in a similar manner to **1a**. Into dry ether (200 ml) was bubbled ammonia gas at −30——40 °C. To the solution was added dropwise freshly distilled benzenesulfenyl-d_5 chloride[14] (73—75 °C/3 Torr, 0.026 mol) in dry ether (30 ml). After addition, the bubbling of ammonia gas was stopped and the reaction mixture was raised to room temperature. Filtration of the reaction mixture and evaporation of solvent afforded an orange crystalline mass, which was recrystallized from hexane to give pale pink plates: mp 123—126 °C; yield 1.26 g (38%). IR (KBr): 3270 cm^{-1} (NH). Found: C, 58.85; H, 4.39; N, 5.68%. Calcd for $C_{12}HD_{10}NS_2$: C, 59.22; H, 4.56; N, 5.76%.

*Generation of **2**.* Sulfenamide **1** (10 mg) was treated in solvent (3 ml) with lead dioxide (0.5 g) and potassium carbonate (0.5 g). After filtration, 0.5 ml of the purple solution was placed in an ESR cell and the solution was degassed by three freeze-and-thaw cycles; then the cell was sealed. ESR spectra were recorded at room temperature.

Spin density calculations were carried out on a FACOM 230-60 computer.

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