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First ESR Spectrum of a Selenoaminyl Radical[1]

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Synopsis. *N*-(*o*-Nitrophenylseleno)-3,5-di-*t*-butylphenylaminyl radical, generated by photolysis of *N*-(3,5-di-*t*-butylphenyl)-*o*-nitrobenzeneselenenamide in the presence of di-*t*-butyl peroxide, has been studied by ESR spectroscopy. The ESR parameters are compared with those for the corresponding sulfur analogue.

Thioaminyl radicals ($R\dot{N}SR'$) have an interesting structure in which a divalent sulfur attaches directly to the radical center. Our ESR spectroscopic studies on a variety of thioaminyls have shown that they are electronically substantially stabilized by conjugative delocalization of the unpaired electron from the nitrogen to the sulfur,[2] and that some thioaminyls can be isolated as pure radical crystals or bydrazine-like dimers.[3–5]

In the extension of these ESR studies our interest was focused on electronically related selenoaminyls ($R\dot{N}SeR'$). However, in contrast to a wide ESR study on thioaminyls, there has appeared no ESR report on selenoaminyls in the literature. In this paper we report the first ESR spectrum of a selenoaminyl.

Results and Discussion

Selenenamides are known to be relatively labile owing to the weak N–Se bonds sensitive to hydrolysis;[6] in particular, the compounds of the type RNHSeR′ are much more labile. This was shown by the repeated failures in obtaining the desired RNHSePh compounds from benzeneselenenyl chloride and RNH_2 (R: alkyl or aryl). However, *o*-nitrobenzeneselenenamide derivatives ($RNHSeC_6H_4\text{-}NO_2\text{-}o$) exhibited high stabilities.[6] That is, the reactions of *o*-nitrobenzeneselenenyl chloride with RNH_2 gave the desired *N*-alkyl- and *N*-aryl-*o*-nitrobenzeneselenenamides (**1**) in 53—67% yields.[7]

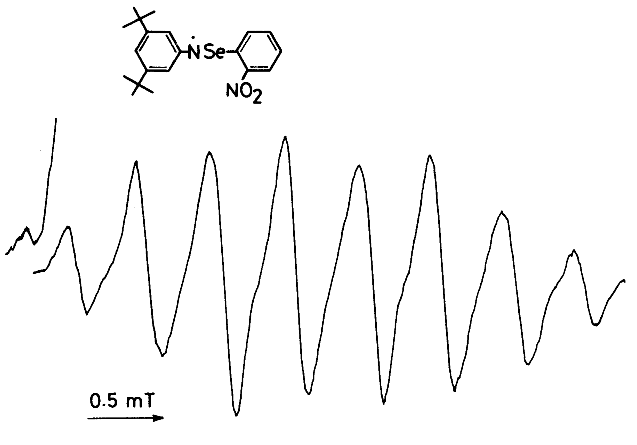
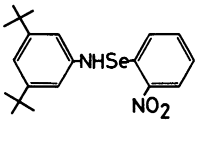
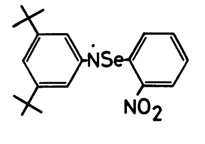


Fig. 1. ESR spectrum of **2a** recorded during photolysis of a solution of **1a** in 1:4 (v/v) di-*t*-butyl peroxide–benzene at 20 °C. The left wing is shown at high gain (5 times), and a satellite line due to ^{77}Se is seen.

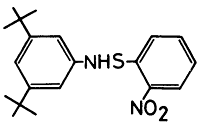

1a


2a

The generation of selenoaminyl radicals was performed by the photolysis of solutions of **1** in the presence of di-*t*-butyl peroxide. When being irradiated in the cavity of an ESR instrument using a 1 kW xenon lamp, a solution of **1a** gave a 1:3:4:4:4:4:3:1 octet ESR spectrum with a relatively broad line width (peak-to-peak width, ca. 0.14 mT) as illustrated in Fig. 1. This signal, upon interruption of the UV-irradiation, disappeared immediately. In cases of other *o*-nitrobenzeneselenenamides,[7] no ESR spectra attributable to the corresponding selenoaminyls were found for the solutions in the temperature range −50—20 °C.

The hyperfine splitting (hfs) constants for **2a**, determined by computer simulation, are a_N: 0.972 (1N), a_H: 0.453 (2H) and 0.525 mT (1H). On the basis of the numbers of the equivalent protons we could readily assign these three protons to the anilino ortho (2H) and para (1H) benzene ring protons. Interestingly, upon recording at higher gain a satellite line due to ^{77}Se (I=1/2, natural abundance 7.6%) was found in the left (low field) wing of the parent spectrum (see, Fig. 1). The assignment of this satellite line was made by its intensity ratio to the parent spectrum (experimental value ca. 3%, theoretical 3.8%). The ESR parameters are listed in Table 1.

For a comparison of the ESR parameters, we also prepared *N*-(*o*-nitrophenylthio)-3,5-di-*t*-butylphenylaminyl (**4**), the corresponding sulfur analogue, by oxidation of *N*-(3,5-di-*t*-butylphenyl)-*o*-nitrobenzenesulfenamide (**3**) with PbO_2. The ESR spectrum is illustrated in Fig. 2. This aminyl, in contrast to the very short-lived **2a** radical, persisted over a long period (> a day) in benzene at room temperature and the radical solution showed a green color [λ_{max} (benzene) 590 nm].[3]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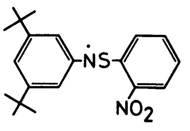
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As found in Fig. 1, there is no splitting due to the phenylseleno benzene ring protons. However, the

Table 1. ESR Parameters for **2a** and Related Aminyls[a, b)]

Radical	a_N	$a_{o\text{-H}}$[c)]	$a_{p\text{-H}}$[c)]	a_{other}	g
2a[d, e)]	0.972	0.453	0.525	0.61 (^{77}Se)	2.011
4[e, f)]	0.958	0.406	0.480	0.074 ($a_{o-\text{H}}$)[g)] 0.088 ($a_{p-\text{H}}$)[g)]	2.0054
5[h)]	0.944	0.565	0.713		

a) Hyperfine splitting constants are given in mT. b) Temperature, 20±2 °C. c) Anilino benzene ring protons. d) Solvent, 1 : 4 (v/v) di-*t*-butyl peroxide-benzene. e) The hyperfine splitting constants are determined by computer simulation. f) Solvent, benzene. g) Phenylthio benzene ring protons. h) Taken from Ref. 11.

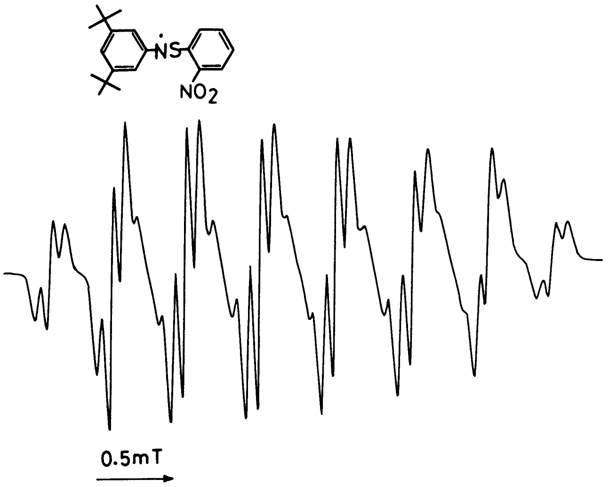


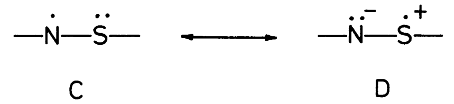
Fig. 2. ESR spectrum of **4** in benzene at 20 °C, generated by oxidation of **3** with PbO$_2$.

unusually high g value (2.011), as well as the relatively high $a_{^{77}\mathrm{Se}}$ value (0.61 mT), is strongly suggestive of a considerable delocalization of the unpaired electron onto the selenium. Because of the large spin-orbit coupling parameter for selenium (1688 cm^{-1}; 382 cm^{-1} for sulfur),[8,9)] the delocalization will cause the ESR lines to be considerably broadened.[10)] Accordingly, small hfs's will have no effect on the spectrum other than to broaden the ESR lines.

When comparing the ESR parameters for **2a** with those for **4**, one will find some interesting differences in the ESR parameters between them. First, in the spectrum of **4** the hfs's of 0.074 and 0.088 mT due to the phenylthio benzene ring protons are found. On the other hand, in that of **2a** no splitting due to the phenylseleno benzene ring protons was detected. Second, the hfs constants for the anilino benzene ring protons of **2a** are 0.045—0.047 mT higher than those for **4**. These differences in hfs constants strongly suggest the lower ability of the selenium to delocalize the unpaired electron. That is, the dipolar canonical structure **B** seems to contribute less to the resonance hybride of **2a** than does the corresponding dipolar canonical structure **D** to the hybrid of **4**.

$$-\dot{\mathrm{N}}-\ddot{\mathrm{Se}}- \longleftrightarrow -\overset{..-}{\mathrm{N}}-\overset{.+}{\mathrm{Se}}-$$

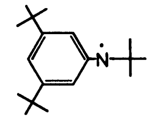
A B



$$-\dot{\mathrm{N}}-\ddot{\mathrm{S}}- \longleftrightarrow -\overset{..-}{\mathrm{N}}-\overset{.+}{\mathrm{S}}-$$

C D

On the other hand, when comparing the ESR parameters for **2a** with those for 3,5,*N*-tri-*t*-butylphenylaminyl (**5**)[11)] which is substituted at the nitrogen by a *t*-butyl group that has a negligibly small ability to delocalize the unpaired electron, one will note that the anilino benzene ring proton hfs constants for **2a** are substantially lower (0.112—0.188 mT) than those for **5** (see: Table 1). The sums of the spin densities on the ortho and para carbons of each anilino benzene ring ($\sum\rho_{o\text{-and }p\text{-C}}$) of **2a**, **4**, and **5**, derived from Table 1 using $Q_{\mathrm{H}}^{\mathrm{CH}}=-2.7$ mT, are 0.530 (**2a**), 0.479 (**4**), and 0.683 (**5**), these magnitudes being strongly suggestive of the order: sulfur>selenium>*t*-Bu for the ability to delocalize the unpaired electron. This order, however, is not in agreement with the report of Gilbert et al.,[8,10)] in which they showed the opposite order: ρ_{Se}^{π} (0.085)>ρ_{S}^{π} (0.076) based on the Hückel MO calculations with McLachlan's perturbation treatment on phenothiazine and phenoselenazine neutral radicals. The discrepancy seemed to come from the choice of parameters used in their calculations. To confirm this point calculations were performed using the same set of parameters as in the literature[8,10)] ($\alpha_{\mathrm{N}}=\alpha+0.8\beta$, $\alpha_{\mathrm{S}}=\alpha+1.25\beta$, $\alpha_{\mathrm{Se}}=\alpha+1.21\beta$, $\alpha_{\mathrm{NO_2\text{-}C}}=\alpha+0.1\beta$, $\beta_{\mathrm{CN}}=1.0\beta$, $\beta_{\mathrm{NS}}=\beta_{\mathrm{CS}}=\beta_{\mathrm{NSe}}=\beta_{\mathrm{CSe}}=0.57\beta$, and $\lambda=0.7$). In the present calculations the molecules are assumed to be planar. The results of the calculations certainly showed the same order as that of Gilbert, et al.: ρ_{Se}^{π} (0.138)>ρ_{S}^{π} (0.127). Although, in the above calculations the magnitude of β_{NS} is taken to be the same as that β_{NSe} and the magnitude of β_{CS} is taken to be the same as that of β_{CSe}, these are not physically realistic because of the loss of overlap due to extension of orbitals in the selenium. We think that k_{NS} and k_{CS} (for $\beta_x=k_x\beta$) should be larger than k_{NSe} and k_{CSe}, respectively. From this viewpoint, the magnitudes of β_{NS} and β_{CS} were changed from 0.57β to 0.65β.[12)] Recalculations using these modified parameters afforded the order ρ_{S}^{π} (0.158)>ρ_{Se}^{π} (0.138), which is in agreement with the experimental results. Consequently, we wish to



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conclude that the ability of selenium to delocalize the unaired electron is lower than sulfur.

Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were run on a JASCO A-202 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL JNM-PS-100 spectrometer and chemical shifts (δ) are expressed in ppm relative to internal tetramethylsilane.

3,5-Di-*t*-butylaniline[13] and *o*-nitrobenzeneselenenyl chloride[14] were prepared by the reported procedures.

***N*-(3,5-Di-*t*-butylphenyl)-*o*-nitrobenzeneselenenamide (1a).** To a stirred solution of 1.00 g (4.87 mmol) of 3,5-di-*t*-butylaniline and 0.73 g (7.2 mmol) of triethylamine in 200 ml of dry ether was added dropwise at 0 °C a solution of 1.00 g (4.23 mmol) of *o*-nitrobenzeneselenenyl chloride in 50 ml of dry ether. After being stirred at the same temperature for 2 h, the reaction mixture was filtered and evaporated under reduced pressure. The residual red solid mass was crystallized from hexane to afford red prisms: mp 160—162 °C; yield 1.11 g (65%); IR (KBr) 3360 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ=1.25 (s, *t*-Bu, 18H), 5.10 (s, NH, 1H), 6.73—8.40 (m, aromatic, 7H). Found: C, 59.44; H, 6.66; N, 6.92%. Calcd for $C_{20}H_{26}N_2O_2Se$: C, 59.25; H, 6.47; N, 6.91%.

***N*-(3,5-Di-*t*-butylphenyl)-*o*-nitrobenzenesulfenamide (3).** To a stirred solution of 2.00 g (9.74 mmol) of 3,5-di-*t*-butylaniline and 1.5 g (15 mmol) of triethylamine in 100 ml of dry ether was added dropwise at 0 °C a solution of 2.2 g (12 mmol) of *o*-nitrobenzenesulfenyl chloride in 100 ml of dry ether. After being stirred at the same temperature for 2 h, the reaction mixture was filtered and evaporated under reduced pressure. The residual orange powdery solid was subjected to column chromatography (alumina, Merck art 1097) using benzene as eluant, and crystallization from benzene–hexane gave yellow prisms: mp 138—140 °C; yield 2.61 g (75%); IR (KBr) 3400 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ=1.26 (s, *t*-Bu, 18H), 5.09 (s, NH, 1H), 6.78—8.37 (m, aromatic, 7H). Found: C, 66.96; H, 7.28; N, 7.54%. Calcd for $C_{20}H_{26}N_2O_2S$: C, 67.01; H, 7.31; N, 7.81%.

ESR Measurements. Radicals **2** were generated by the photolysis of solutions of 10—25 mg of **1** in 0.20 ml of 1 : 4 (v/v) di-*t*-butyl peroxide-benzene (or toluene) using a 1 kW xenon lamp. Aminyl **4** was generated by treating 50 mg of **3** in 3 ml of benzene with 2 g of PbO_2. All the solutions were degassed by three freeze-pump-thaw cycles using a high vacuum system. ESR spectra were recorded on a JEOL JES-FE-2XG spectrometer equipped with an X-band microwave unit and 100 kHz field modulation. Hyperfine splitting constants and g values were determined by a comparison with Fremy's salt in an aqueous K_2CO_3 solution (a_N=1.309 mT, g=2.0057). Estimated accuracy for the hfs constants, ±0.01 mT.

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7) We also prepared, besides **1a**, *N*-(*p*-*t*-butylphenyl)-(**1b**), *N*-*t*-butyl-(**1c**), and *N*-(1-adamantyl)-*o*-nitrobenzeneselenenamides (**1d**) in a similar manner. The melting points, yields, IR (KBr) and ^{1}H NMR ($CDCl_3$) data of these compounds are as follows: **1b**: red plates with mp 131—133 °C (crystallized from hexane); yield 53%; IR 3330 cm^{-1} (NH); ^{1}H NMR δ=1.27 (s, *t*-Bu, 9H), 5.05 (s, NH, 1H), 6.77—8.41 (m, aromatic, 8H). **1c**: orange prisms with mp 42—43 °C (crystallized from hexane); yield 67%; IR 3320 cm^{-1} (NH); ^{1}H NMR δ=1.24 (s, *t*-Bu, 9H), 2.91 (s, NH, 1H), 7.16—8.51 (m, aromatic, 4H). **1d**: orange needles with mp 74—76 °C (crystallized from hexane); yield 59%; IR 3290 cm^{-1} (NH); ^{1}H NMR δ=1.61—2.04 (m, adamantyl, 15H), 2.86 (s, NH, 1H), 7.18—8.60 (m, aromatic, 4H).

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