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^{1}H, ^{13}C, ^{15}N, ^{17}O and ^{77}Se NMR of Selenenamides

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Numerous areneselenenamides derived from ammonia, primary and secondary amines and two *N*,*N*-bis(arylseleno)alkylamines have been studied. The selenenamides bearing an electron-withdrawing substituent on the aromatic moiety are stable. The ^{1}H, ^{13}C and ^{77}Se chemical shifts and some coupling constants are reported.

For *N*,*N*-dialkyl-*o*-nitrobenzeneselenenamides, the ^{77}Se NMR and the ^{17}O NMR give evidence of an Se–O interaction. In *N*-alkyl derivatives, a hydrogen bond between the amine group and the *ortho*-substituent is proposed to explain the deshielding of the selenium nucleus.

KEY WORDS ^{1}H, ^{13}C, ^{15}N, ^{17}O and ^{77}Se NMR selenenamides Se–O interactions hydrogen bonding

INTRODUCTION

The ^{77}Se NMR of organoselenium compounds is now well documented.[1-5] To our knowledge, however, except for some chemical shift values given by Reich *et al.*,[6,7] nothing is known about the ^{77}Se NMR of selenenamides. This is because the easy hydrolysis of these compounds makes them difficult to study.[6-20] We have recently observed that selenenamides derived from morpholine are more stable.[16,17] As electron-withdrawing groups in comparable structures[21-23] increase the stability, especially when they are in the *ortho*-position, we were able to prepare some stable areneselenenamides **1** and to obtain the crystallographic data for the morpholino-*o*-nitrobenzeneselenenamide (**1h**).[24] Other selenenamides were prepared without purification immediately prior to their NMR analysis. All the compounds studied are presented in Table I.

EXPERIMENTAL

In order to study the structures of these compounds their ^{1}H, ^{13}C and ^{77}Se NMR spectra have been analysed; in addition, for the nitro derivatives **1h** and **1j**, the ^{15}N and ^{17}O NMR spectra were investigated.

NMR measurements

Proton NMR spectra were obtained at 60 MHz with TMS as internal reference and $CDCl_3$ as solvent. ^{13}C and ^{77}Se NMR spectra were recorded on samples at 1 M concentration in $CDCl_3$ at 27 °C, unless stated otherwise.

^{13}C NMR spectra were recorded on a Bruker WP80 spectrometer at 20.11 MHz. The carbon resonance of $CDCl_3$ was taken as a secondary reference at 76.91 ppm from TMS. The carbon–carbon coupling constants presented in Fig. 1 were obtained from proton decoupled spectra at 100.57 MHz. The ^{77}Se NMR spectra were obtained on a Bruker WH 90 spectrometer with multinuclear facilities at 17.19 MHz and referred to neat dimethylselenide using the substitution method.[25] High-frequency resonances (deshielding) have positive chemical shifts according to the IUPAC convention.[26] The selenium signal was obtained from proton decoupled spectra. In some cases, $Cr(acac)_3$ was added to obtain quaternary carbon resonances without influencing the ^{13}C and ^{77}Se chemical shifts. All selenium spectra were run at least twice on different samples.

^{17}O NMR resonances were observed at 54.24 MHz with water as external reference and ^{15}N NMR signals were recorded at 40.56 MHz from proton decoupled spectra. The chemical shifts refer to nitromethane as the external reference.

Preparation of compounds

The selenenyl bromides used for the synthesis of the selenenamides were prepared from the corresponding diselenides and bromine,[27] and by debromination of the selenenyl tribormide in the case of *p*-nitrobenzeneselenenyl bromide.[8] *o*-Acetylbenzeneselenenyl bromide[28] was obtained from the selenocyanate synthesized by the classical method.[29] All stable compounds gave correct elemental analyses and mass spectra.

Preparation of the selenenamides 1, 2 and 3. The areneselenenyl bromide (1 mmol) was dissolved in hexane (50 ml) or in hexane–methylene chloride (90 : 10) for the nitro-substituted areneselenenyl bromides. The

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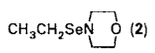
Table 1. Structures and δSe values of the compounds studied

$ArSeNR_2$ (1)

	Ar	R,R	δSe
a	C_6H_5	CH_3, CH_3	924.2
b	$(o)NO_2C_6H_4$	CH_3, CH_3	909.5
c	$(p)NO_2C_6H_4$	CH_3, CH_3	903.5
d	C_6H_5	C_2H_5, C_2H_5	—
e	C_6H_5	$-(CH_2)_5-$	913.0
f	$(o)NO_2C_6H_4$	$-(CH_2)_5-$	885.8
g[a]	C_6H_5	Morpholino	926.1
h[a]	$(o)NO_2C_6H_4$	Morpholino	892.8
i[a]	$(m)NO_2C_6H_4$	Morpholino	910.4
j[a]	$(p)NO_2C_6H_4$	Morpholino	893.8
k[a]	$(o)CH_3COC_6H_4$	Morpholino	908.3
l[a]	$(p)ClC_6H_4$	Morpholino	917.5
m[a]	2-pyridyl	Morpholino	913.5



(2)

δSe = 870.1

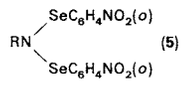
ArSeNHR (3)

	Ar	R	δSe
a	C_6H_5	n-C_5H_9	737.8
b	$(o)NO_2C_6H_4$	n-C_4H_9	765.5
c	$(p)NO_2C_6H_4$	n-C_4H_9	735.4
d	C_6H_5	t-C_4H_9	616.9
e	$(o)NO_2C_6H_4$	t-C_4H_9	671.6
f	$(p)NO_2C_6H_4$	t-C_4H_9	634.3
g	$(o)NO_2C_6H_4$	C_6H_{11}	724.6
h	$(o)NO_2C_6H_4$	$C_6H_4CH_3(p)$	758.3
i	$(o)CH_3COC_6H_4$	t-C_4H_9	676

[a] 

$ArSeNH_2$ (4)

	Ar	δSe
a	$(o)NO_2C_6H_4$	683.0
b	$(p)NO_2C_6H_4$	614.8



(5)

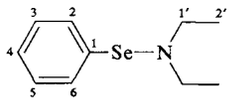
	R	δSe
a	n-C_4H_9	911.0
b	t-C_4H_9	912.0

ArSeY (6)

	Ar	Y	δSe
a	C_6H_5	CN	319
b	$(o)NO_2C_6H_4$	CN	413
c	C_6H_5	Br	867
d	$(o)NO_2C_6H_4$	Br	908

amine (2 mmol) in hexane was added dropwise at room temperature with stirring under an inert gas. The solution rapidly became clear, and after 30 min the ammonium salt formed was eliminated. Compounds **1a**, **1d** and **2** were concentrated under vacuum without heating; the remaining oil was distilled under low pressure for **1a**, **1d**, **1e** and **1g**. For the other compounds the solid formed was crystallized from hexane.

The physical constants are given in the following order: yield (%); melting point (°C) or boiling point (°C/mmHg); NMR spectra, (δ in ppm). Carbon numbering is shown below.



1a: 62%; 40 °C/0.1 mmHg; ^{1}H NMR, 2.78 (6H), 7.2-7.6 (5H); ^{13}C NMR, C-2,6 = 133.9, C-3,5 = 127.9, C-4 = 128.2, C-1′ = 50.7. **1d**: 59%; 64 °C/0.4 mmHg; ^{1}H NMR, 1.16 (6H), 2.96 (4H), 7.2-7.7 (5H). **1e**: 75%; 95 °C/0.3 mmHg; ^{1}H NMR, 1.2-1.8 (6H), 2.85-3.2 (4H), 7.15-7.8 (5H); ^{13}C NMR, C-1 = 127.2, C-2,6 = 133.6, C-3,5 = 128.3, C-4 = 127.8, C-1′ = 59.3, C-2′ = 27.6, C-3′ = 23.0. **1g**: 77%; 110 °C/0.4 mmHg; ^{1}H NMR, 3.02 (4H), 3.70 (4H), 7.3-7.8 (5H); for ^{13}C data see Fig. 1. **1h**: 91%; 82 °C; ^{1}H NMR, 3.25 (4H), 3.77 (4H), 7.2-7.9 (2H), 8.2-8.5 (2H); for ^{13}C data see Fig. 1. **1i**: unstable oil; ^{1}H NMR, 3.10 (4H), 3.75 (4H), 7.3-8.7 (4H); ^{13}C NMR, C-1 = 131.5, C-2 = 124.9, C-3 = 148.0, C-4 = 121.9, C-5 = 129.2, C-6 = 136.2, C-1′ = 68.4, C-2′ = 58.0. **1j**: 88%; 89 °C; ^{1}H NMR, 3.22 (4H), 3.72 (4H), 7.67 (2H), 8.17 (2H) (J_{ortho} = 8.3 Hz); for ^{13}C data see Fig. 1. **1k**: 80%; 97 °C; ^{1}H NMR, 2.60 (3H), 3.12 (4H), 3.76 (4H), 7.10-7.75 (2H), 8.0 (1H), 8.4 (1H). **1l**: 86% 44 °C; ^{1}H NMR, 2.97 (4H), 3.67 (4H), 7.4 (2H), 7.5 (2H), (J_{ortho} = 8.1 Hz); ^{13}C NMR, C-1 = 127.3, C-2,6 = 135.1, C-3,5 = 128.8, C-4 = 134.0, C-1′ = 68.2, C-2′ = 58.2. **1m**: unstable oil; ^{1}H NMR, 3.25 (4H), 3.6-3.9 (4H), 6.9-8.6 (4H); ^{13}C NMR, C-3 = 149.6, C-4 = 120.2, C-5 = 122.0, C-6 = 136.3, C-1′ = 68.5, C-2′ = 58.7. **3a**: not obtained in pure form; ^{1}H NMR, 0.8-1.7 (7H), 2.20 (NH), 2.96 (2H), 7.2-7.7 (5H). **3b**: 90%; 24 °C; ^{1}H NMR, 0.9-1.9 (7H), 2.75 (NH), 3.1 (2H), 7.2-7.8 (2H), 8.2-8.5 (2H). **3e**: 88%; 33 °C; ^{1}H NMR, 1.22 (9H), 2.90 (NH), 7.3-7.7 (2H), 8.1-8.5 (2H); ^{13}C NMR, C-3,4 = 125.3, C-5 = 132.2, C-6 = 127.6, C-1′ = 54.2, C-2′ = 30.1. **3f**: 86% 62 °C; (NMR ^{1}H) 1.22 (9H), 3.30 (NH), 7.7 (2H), 8.16 (2H), (J_{ortho} = 8.3 Hz); ^{13}C NMR, C-2,6 = 125.4, C-3,5 = 123.4, C-1′ = 54.9, C-2′ = 29.8. **3g**: 92%; 44 °C; ^{1}H NMR, 0.9-2.30 (10H), 2.4-3.0 (2H), 7.1-7.8 (2H), 8.2-8.5 (2H); ^{13}C NMR, C-3 = 125.3, C-4 = 125.5, C-5 = 133.3, C-6 = 127.2, C-1′ = 60.0, C-2′ = 35.2, C-3′ = 25.0, C-4′ = 25.6. **3h**: 95% 125 °C; ^{1}H NMR, 2.25 (3H), 5.07 (NH), 6.9-8.0 (6H), 8.2-8.5 (2H); ^{13}C NMR, C-3 = 125.8, C-4 = 126.2, C-5 = 135.2, C-6 = 126.3, C-1′ = 143.9, C-2′ = 115.6, C-3′ = 129.8, CH_3 = 20.2. **3i**: not obtained in pure form; ^{1}H NMR, 1.22 (9H), 2.60 (3H), 7.1-7.7 (2H), 7.95 (1H), 8.60 (1H).

Preparation of the selenenamides 4. The selenenamides **4a**[30] and **4b**[31] were prepared by bubbling ammonia into a solution of the selenenyl bromide in hexane and were isolated in the same way as were the other selenenamides. The physical constants are depicted as for **1** and **3**. **4a**: 78%; 224 °C; ^{1}H NMR, 2.55 (NH_2), 7.55-9.0 (4H); ^{13}C NMR, C-3,4 = 125.4, C-5 = 133.6, C-6 = 126.6. **4b**: 83%; 183 °C; ^{1}H NMR, 2.80 (NH_2), 7.20 (2H), 8.10 (2H); ^{13}C NMR, C-2 = 128.2, C-3 = 121.5, C-4 = 144.3, C-5 = 121.5, C-6 = 128.2 (in DMSO-d_6).

Preparation of *N*,*N*-bis(*o*-nitrophenylseleno)alkylamines 5. A solution of the selenenamide **3b** or **3d** (2 mmol) in hexane (10 ml) was added dropwise at room temperature under

a nitrogen atmosphere to a solution of *o*-nitrobenzeneselenenyl bromide (1 mmol) in hexane–methylene chloride (90:10) (50 ml). After stirring for 1 h the bromide corresponding to the selenenamide **3** was elimimated. After low-pressure concentration the solution gave a solid which was recrystallized twice from hexane. The physical constants are as follows. **5a**: 68%; 132 °C; ^{1}H NMR, 0.9–1.9 (7H), 3.8 (2H), 7.4–8.5 (8H). **5b**: 63%; 112 °C; ^{1}H NMR, 1.46 (9H), 7.4–8.5 (8H).

RESULTS AND DISCUSSION

No information can be deduced from the ^{1}H spectra. The highly shielded signals of the amino protons for **3** and **4** should be noted.

The assignment of the aliphatic carbons is in agreement with the literature.[32] The resonances of the unsubstituted aromatic carbons were assigned according to previous work.[12,33,34]

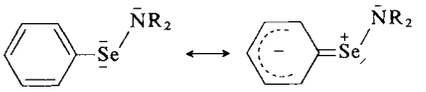
The use of substituent increments[35] for the phenyl ring carbons allows an unambiguous assignment except for the *o*-nitrophenyl group. In these cases we used the $J(CC)$ values deduced from the satellites in the proton-decoupled carbon spectra. Owing to the differences in these values it is easy to assign the resonances of the aromatic ring carbons. The results are presented in Fig. 1, but the ^{13}C spectra are not of structural value.

^{77}Se NMR spectra

The ^{77}Se chemical shifts referred to neat Me_2Se are presented in Table 1, where some chemical shifts of selenocyanates **6a** and **6b** and selenenyl bromides **6c** and **6d** are added for comparison. No results are given for **1d** since very different values were observed depending on the method of preparation of the samples.

In *o*-nitrobenzeneselenenamide (**4a**) the presence of an NH_2 group was demonstrated using proton coupled ^{77}Se spectra. A triplet is observed [$^{2}J(SeH) = 8$ Hz], each line being slightly split into a doublet (*ca.* 3 Hz) arising from coupling with the *ortho* phenyl proton. The $^{2}J(SeH)$ value falls in the usual range for this parameter.[1,5]

The ^{77}Se NMR results are interesting. The Se atom is highly deshielded, especially in *N,N*-disubstituted molecules, compared with the resonances of other divalent selenium compounds such as selenides, diselenides and selenocyanates.[1,5] This deshielding may be partially explained by the electronegativity of the nitrogen atom, which usually has the same effect on a neighbouring carbon atom,[32] but also by the possible double bond character of the Se—C linkage resulting from the mesomeric form B depicted below.

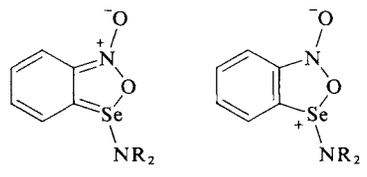


These factors are normally invoked to explain large deshielding effects in ^{77}Se NMR,[36,37] as in areneselenenyl bromides **6c**, **6d**. This double bond character is also suggested by X-ray measurements carried out on the selenenamide **1h**.[24] The Se—C bond length (0.1916 nm) is found to be shorter than that of a single Se—C bond.[38]

For *N,N*-disubstituted selenenamides **1** the nitrogen substituent effect is very limited, as shown by the selenium resonance in **1a**, **1e** and **1g**, but variations do occur with the nature of the aryl selenium group. The exchange of a phenyl group for an ethyl group (**1g**→**2**) leads to a shielding of about 50 ppm which is less, however, than that observed for some other molecules.[5,39]

Substitution of the aromatic ring in compounds **1** does not greatly influence the selenium chemical shift for a given nitrogen group. The situation changes with *N*-substituted selenenamides **3a–3b** and **3d–3e**, where the presence of an *ortho* nitro group leads to a large deshielding effect also observed for selenenyl bromides **6c** and **6d** and for selenocyanates **6a** and **6b**. Conversely, with *N,N*-disubstituted selenenamides **1a–1b**; **1e–1f**; **1g–1h**, the change from a proton to an *ortho* nitro group leads to a small shielding effect.

This particular behaviour sometimes involves a specific interaction between the nitro group and the selenium atom. As previously proposed for other *o*-nitrophenylselenium compounds,[23] the cyclic forms depicted below could account for this result. A similar shielding effect is, however, observed for the *p*-nitrobenzeneselenenamide **1j**, and a possible explanation is the



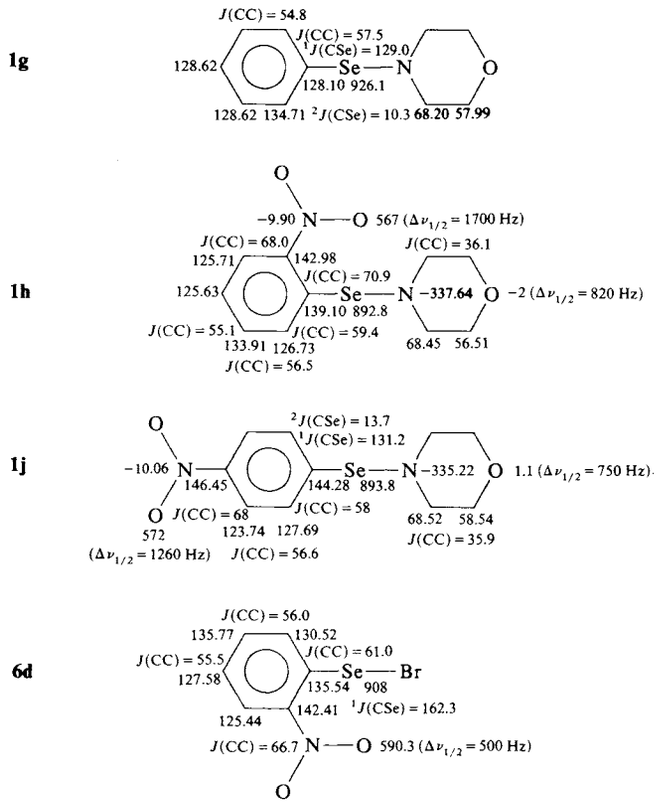


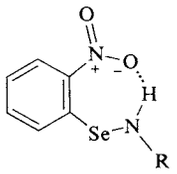
Figure 1. ^{13}C, ^{15}N, ^{17}O and ^{77}Se chemical shifts and coupling constants for some of the compounds studied.

existence of dimeric interactions. As proposed in several publications,[40-43] a non-bonded interaction exists in analogous structures having an arylseleno group bearing a carbonyl or a nitro group in the *ortho* position. On the other hand, in the solid state the selenenamide **1h** shows two different N—O bond lengths in the nitro group[24] and a distance for Se···O of 0.2576 nm. This value is intermediate between the sum of the van der Waals radii (0.34 nm) and the Se—O covalent bond length (0.17 nm).

In order to obtain more information the ^{15}N and ^{17}O NMR spectra of the *o*- and *p*-nitrobenzeneselenenamides **1h** and **1j** were recorded. The results are shown in Fig. 1. The ^{15}N NMR resonances are at the usual value is intermediate between the sum of the van der fall in the usual chemical shift range without any visible splitting into two resonances, the line widths are about twice the normal values observed for an *ortho*-nitro group,[44] even in the case of the selenenyl bromide **6d**. This ususual line width for an *ortho*-nitro group with the observation of two different oxygen atoms in the solid state[24] seems to reflect a particular interaction between the selenium atom and one oxygen atom of the nitro group.

The selenium chemical shifts of *N*-substituted selenenamides **3** are upfield of those of the *N,N*-disubstituted derivatives **1**. This behaviour is similar to that of selenides in which an α-methyl group is replaced by a proton. For instance, in the sequence ter-butylmethylselenide [$CH_3SeC(CH_3)_3$: $\delta = 294$ ppm], ethylmethylselenide ($CH_3SeCH_2CH_3$: $\delta = 108$ ppm) and dimethylselenide (CH_3SeCH_3: $\delta = 0$ ppm) the increment is approximately 100 ppm per methyl group linked to the α-carbon. Here a similar order is observed between **1**, **3** and **4**.

For *N*-substituted selenenamides **3**, substitution by an electron-withdrawing group (NO_2) generally leads to deshielding. Moreover, the *ortho* and *para* substituents have different effects. This result can be explained by the existence of a chelation, as depicted below. This internal hydrogen bond has a higher energy than that involved in the interaction between the oxygen atom of the nitro group and the selenium atom, discussed above for the selenenamides **1**.



The selenium chemical shifts in **3b**, **3e** and **3g** demonstrate a shielding effect of 40–50 ppm when a proton linked to the α-carbon of the amino group is replaced by an alkyl substituent. This β-effect relative to the selenium resonance has previously been observed in other selenium compounds, having the same direction and simlar amplitudes.[45]

The two di(arylseleno)amines **5a** and **5b** have selenium chemical shifts in the range found for *N,N*-dialkylselenenamides **1**.

CONCLUSIONS

Areneselenenamides with various nitrogen substituents have been prepared from areneselenenyl bromides, and some are stable. Their ^1H, ^{13}C and ^{77}Se NMR parameters are reported and, in some cases, the ^{17}O and ^{15}N data. The introduction of an electron-withdrawing substituent, especially a nitro group in the *ortho* or in the *para* position of the aromatic moiety, increases the stability. The selenium and oxygen NMR results show that there is a weak interaction between the *ortho* substituent and the selenium atom in *N,N*-disubstituted selenamides which increases this stability. For *N*-alkylated *ortho*-substituted areneselenenamides **3** and for the selenenamide **4a**, which are also stable compounds, the deshielding effect observed for the selenium resonance can be explained by a chelation which influences the selenium-substituent interaction.

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