

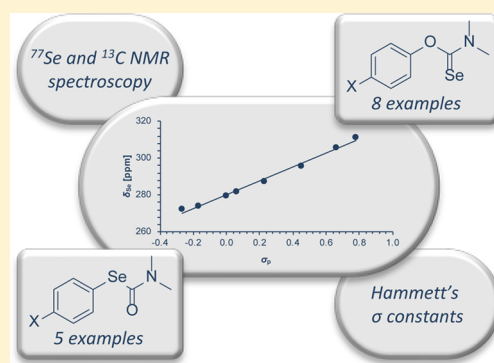
⁷⁷Se NMR Spectroscopy As a Sensitive Probe for Hammett σ Constants

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S Supporting Information

ABSTRACT: Herein we showcase the use of a combination of ¹H, ¹³C, and ⁷⁷Se NMR spectroscopy as a sensitive tool for correlation analysis. A series of substituted O-aryl selenocarbamates [ArOC(Se)N(CH₃)₂] and Se-aryl selenocarbamates [ArSeC(O)N(CH₃)₂] have been investigated by means of ¹H, ¹³C, and ⁷⁷Se NMR spectroscopy. We have determined the ¹H, ¹³C, and ⁷⁷Se chemical shift values as well as both one- and two-bond heteronuclear ¹³C–⁷⁷Se coupling constants, and the changes in both the chemical shift values and the coupling constants were found to obey linear free energy relationships with Hammett's σ_p and σ_p^- constants. For the eight studied O-aryl selenocarbamates, we observe linear free energy correlations with two of the ¹³C and ⁷⁷Se chemical shift values and as well as one ¹³C–⁷⁷Se coupling constant. With the five examples of Se-aryl selenocarbamates, linear correlations are observed with three different ¹³C–⁷⁷Se coupling constants. The strong internal consistency validates the use of ⁷⁷Se NMR spectroscopy for correlation analysis.



INTRODUCTION

Correlations between thermodynamic and kinetic parameters are important for elucidating reaction mechanisms, and the relationship between parameters known as substituent constants, which appear in linear free energy expressions, and various directly measurable quantities has received significant attention.¹ Such correlations are often discussed using the various Hammett substituent constants, such as σ , σ^+ , and σ^- .^{2,3}

Over the years, numerous studies have shown how Hammett substituent constants can correlate linearly with not only reaction rates and equilibrium constants but also infrared frequencies, ultraviolet absorption spectra, and NMR spectral parameters of various conjugated compounds. This free energy correlation is not surprising since Hammett substituent constants are a measure of the relative effect of the substituents on the electron density at the studied site and should therefore be able to correlate with other properties that reflect the electron distribution within the molecule. Through this connection, it is possible to gain knowledge of reaction mechanisms and structure–property relationships, two concepts that are fundamental in chemistry.^{4–6}

¹H and ¹³C chemical shift values are frequently used for the study of the transmission of electronic effects of substituents in conjugated organic molecules.^{7–9} Since the electron density around the nucleus of interest is mostly affected by the electron-donating or -withdrawing ability of the substituent, a correlation, based on the theory of linear free energy relationships, between the observed chemical shifts (δ_X) and Hammett substituent constants (σ) can be found (eq 1),

$$\delta_X = \rho\sigma + \delta_0 \quad (1)$$

where ρ is a constant reflecting the sensitivity of the chemical shift values to the substituents while δ_0 is the chemical shift value of the unsubstituted compound.¹⁰ Obtaining good correlations with eq 1 would indicate that the substituent effects on the chemical shift values of the studied compounds are electronic in origin.

Coupling constants are another major parameter obtained by NMR spectroscopy that has shown to be able to obey linear free energy relationships with Hammett's σ constants of the substituents.^{11,12} In general, the magnitude of a coupling constant depends on the number of bonds intervening between the two interacting atoms or groups of atoms. In addition, the electronegativity of potential attached atoms or groups together with stereochemical influence also plays a significant role. Further, it is not unusual for the coupling constants to depend on the hybridization of the atoms involved.^{13,14} Since the coupling constant is a physical parameter that is expressed as a function of the electronic distribution within the molecule it will also reflect differences in the electronic structure brought about by the presence of different substituents. This correlation can be expressed as a linear free energy relationship in the same manner as in eq 1.

It is important that the change of the physical parameter that is monitored is convincingly large when constructing Hammett plots. Data obtained using ¹H and ¹³C NMR spectroscopy is often used as the input to Hammett plots, and

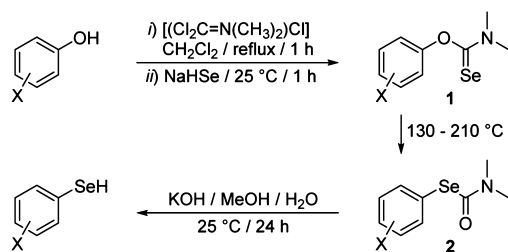
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a particular weakness of this strategy is the often small change in chemical shift values or coupling constants that is observed. An attractive approach would therefore be to make the measurements on nuclei with a wider range. This is a possibility when working with organoselenium compounds. Selenium has six naturally occurring isotopes where only one of them, ^{77}Se (7.58%), is NMR active having a nuclear spin quantum number of $I = 1/2$. ^{77}Se resonances are known to show a remarkable sensitivity toward small changes in the electronic structure of the selenium atom and its directly bonded atom which is why they appear in a wide range of about 3000 ppm. In addition, the ^{13}C – ^{77}Se coupling constants vary from 45 to 250 Hz and the ^1H – ^{77}Se coupling constants are shown in a range of 60 Hz. All this makes ^{77}Se NMR spectroscopy a very sensitive tool for the analysis of organoselenium compounds.¹³

The development of organoselenium chemistry has been relatively slow as compared to other classes of organic chemistry. However, selenium containing compounds are attractive synthetic targets because of their ability to participate in chemo-, regio-, and stereoselective chemical reactions, and in addition, they are found to be useful in a range of biological activities where they are often present in the form of selenocysteine, the seleno analogue of cysteine.¹⁵

In our previous work we presented the first thermally induced $\text{O}_{\text{Ar}} \rightarrow \text{Se}_{\text{Ar}}$ migration reaction that led to the rearrangement of a range of substituted *O*-aryl selenocarbamates **1** [$\text{ArOC}(\text{Se})\text{N}(\text{CH}_3)_2$] into the corresponding *Se*-aryl selenocarbamates **2** [$\text{ArSeC}(\text{O})\text{N}(\text{CH}_3)_2$] (Scheme 1).¹⁶ The

Scheme 1. Synthesis of an Arylselenol (Isolated As the Diselenide) From the Corresponding Phenol via the Seleno Newman–Kwart Rearrangement



rearrangement protocol enabled the preparation of arylselenols containing a wide variety of functional groups from the corresponding phenols in three convenient steps. Our focus was back then on studying the reaction mechanism of the seleno Newman–Kwart rearrangement, and we therefore simply analyzed the compounds by ^1H and ^{13}C NMR spectroscopy. However, the development of the seleno Newman–Kwart rearrangement gave convenient access to a series of *O*-aryl selenocarbamates and *Se*-aryl selenocarbamates with electron-donating and -withdrawing substituents situated on the aromatic ring. These substituents are ideally situated to study a variety of phenomena with respect to the linear free energy relationship using different Hammett substituent constants.

In this paper, we demonstrate convincing linear free energy relationships between Hammett's σ_p and σ_p^- constants of the substituents and the ^{13}C and ^{77}Se chemical shift values as well as various ^{13}C – ^{77}Se coupling constants of the *O*-aryl and *Se*-aryl selenocarbamates. These correlations are found by

utilizing the sensitivity of ^{77}Se NMR spectroscopy which is used in an interplay with ^{13}C NMR spectroscopy.

RESULTS AND DISCUSSION

The studied *O*-aryl selenocarbamates **1** and *Se*-aryl selenocarbamates **2** are given in Table 1 together with the

Table 1. Overview of the Studied *O*-Aryl Selenocarbamates **1 and *Se*-Aryl Selenocarbamates **2** Together with the Corresponding Hammett's σ_p and σ_p^- Constants of the Substituents⁵**

X =		
	σ_p	σ_p^-
NO_2	0.78	1.27
CN	0.66	1.00
CO_2CH_3	0.45	0.45
Br	0.23	0.25
F	0.06	–
H	0.00	0.00
CH_3	–0.17	–
OCH_3	–0.27	–

corresponding Hammett's σ_p and σ_p^- constants for the aromatic substituents.⁵ All compounds were analyzed by ^{13}C and ^{77}Se NMR spectroscopy and a detailed description hereof is presented in the Experimental Section.

The sensitivity of ^{77}Se NMR spectroscopy was easily witnessed in our systems where we observed a more than 200 ppm downfield shift of the selenium resonances going from compound **1** to **2** (Figure 1a). This large change shows the altered environment for the selenium atom going from a $\text{C}=\text{Se}$ double bond in **1** to two single $\text{C}–\text{Se}$ bonds in **2**. Additionally, changes in chemical shift values were found depending on the substituent on the aromatic ring. In compound **1** the selenium chemical shifts ranged from δ_{Se} 272 ppm ($\text{X} = \text{OCH}_3$) to δ_{Se} 311 ppm ($\text{X} = \text{NO}_2$) while in **2** the signals were observed in the range δ_{Se} 516 ppm ($\text{X} = \text{H}$) to δ_{Se} 524 ppm ($\text{X} = \text{NO}_2$). These values were found to correlate with Hammett's σ_p and σ_p^- constants, although the correlation coefficient for **2** was not excellent ($R^2 = 0.999$ and 0.702 ; Figure 2a and 2b). Both plots have positive ρ values showing how the selenium resonances vary with the character of the substituents. Electron-donating groups cause upfield shifts due to increased shielding of the selenium nucleus while electron-withdrawing groups cause downfield shifts showing how the electronic effects of the substituents attached to the aromatic ring play a predominant role in the change of the selenium chemical shifts. Such sensitivity of the ^{77}Se resonances makes it very suitable for the elucidation of some fine detail in the structure of organoselenium compounds.

Analyzing the ^{13}C NMR spectra of compound **1** and **2** it was clear that also the chemical shift values of the ^{13}C nuclei changes significantly depending on the substituent attached to the aromatic ring (Figure 1b). Plotting the resonance of the

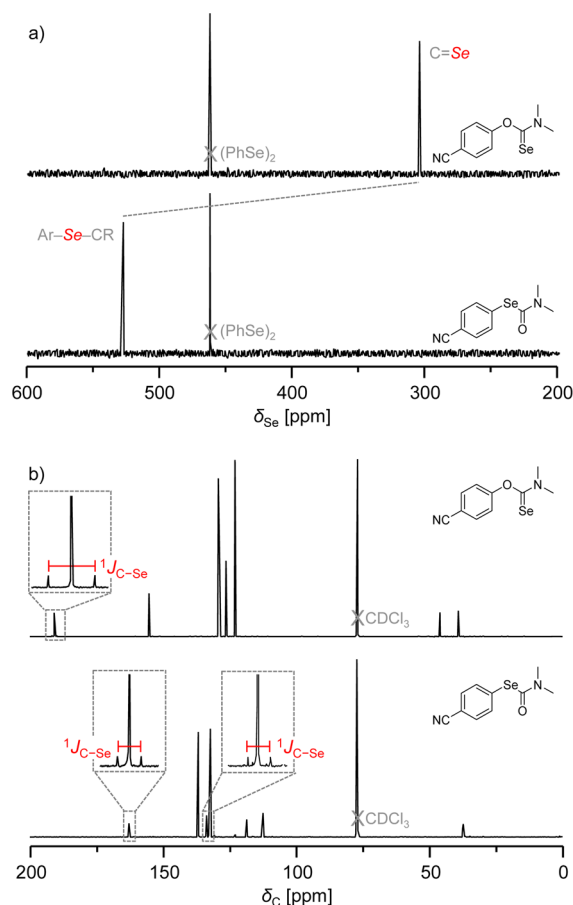


Figure 1. ^{77}Se NMR spectra (57 MHz, CDCl_3 with a saturated solution of $(\text{PhSe})_2$ in CDCl_3 in a sealed tube as external standard) (a) and ^{13}C NMR spectra (125 MHz, CDCl_3) (b) of *O*-(4-cyanophenyl) *N,N*-dimethylselenocarbamate (**1**, $\text{X} = \text{CN}$) and *Se*-(4-cyanophenyl) *N,N*-dimethylselenocarbamate (**2**, $\text{X} = \text{CN}$).

selenocarbamate (**1**) or carbamate (**2**) carbon atom against Hammett's σ_p or σ_p^- constants gave linear correlations for both compounds with similar ρ values ($R^2 = 0.979$ and 0.961 ; Figure 2c and 2d). However, it should be noted that ρ for these plots are negative. A negative sign for ρ is indicative of a reverse substituent chemical shift effect; that is, electron-donating substituents move the carbon resonance downfield and the stronger the electron-donating power of the substituent the lower the field at which the carbon resonance is observed.

The *O*-aryl selenocarbamates **1** appear with ^{13}C resonances for the selenocarbamate at $\delta_{\text{C}} 189.5\text{--}191.5$ ppm while the ^{13}C resonance for the carbamate in **2** is moved ~ 25 ppm upfield to $\delta_{\text{C}} 162.7\text{--}164.7$ ppm. This change in chemical shift values can be explained by considering the altered energy barrier for the internal rotation about the C–N carbamate bond going from **1** to **2**. The rotational barrier is known to be larger for selenoamides compared to amides, as there is a decreasing tendency for selenium to participate in π -double bonds compared to oxygen.¹⁷ The ^{13}C carbamate chemical shifts of **1** are therefore less shielded due to a larger contribution from resonance form B (Scheme 2). This variation in the internal rotational barrier between compound **1** and **2** is also observed in both the ^1H and ^{13}C NMR spectra of these compounds. While in compound **1** the energy barrier is sufficiently high to allow observation of two different sets of signals for the *N,N*-

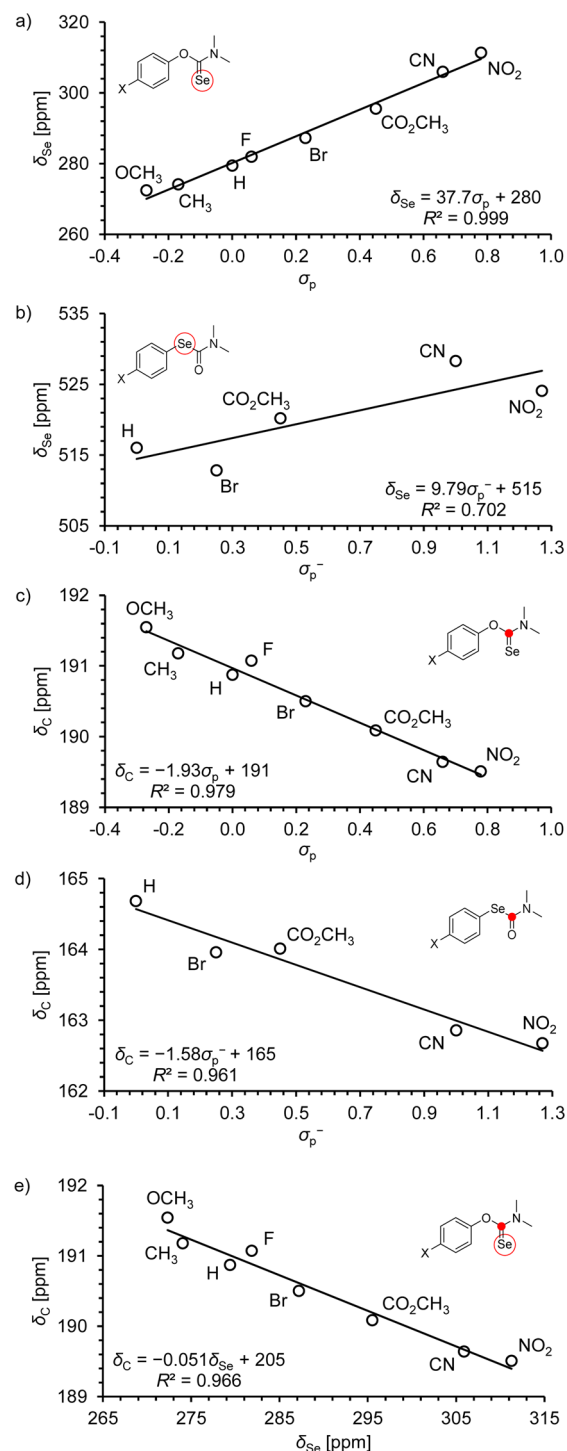
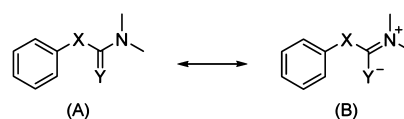


Figure 2. Hammett correlations found between the ^{77}Se and ^{13}C chemical shift values (δ_{X}) and Hammett substituent constants (σ_p or σ_p^-) of *O*-aryl selenocarbamate **1** and *Se*-aryl selenocarbamate **2** (a–d) together with a graph correlating the ^{13}C chemical shifts of the selenocarbamate in **1** with the ^{77}Se chemical shifts (e).

Scheme 2. Two Contributing Resonance Structures of the Carbamate Functionality



dimethylamino group at 25 °C, the rotation barrier in **2** is lower, which is why the two peaks approach each other and thereby form a broad singlet (Figures S3 and S4). A similar upfield shift of the ^{13}C resonances as the one in the selenocarbamate **1** is observed when comparing with the corresponding thiocarbamates (δ_{C} 186.4–188.5 ppm) and carbamates (δ_{C} 153.4–155.3 ppm)¹⁸ that are shown in Figure 3. Accordingly, the ^{13}C resonances for the carbamates appear

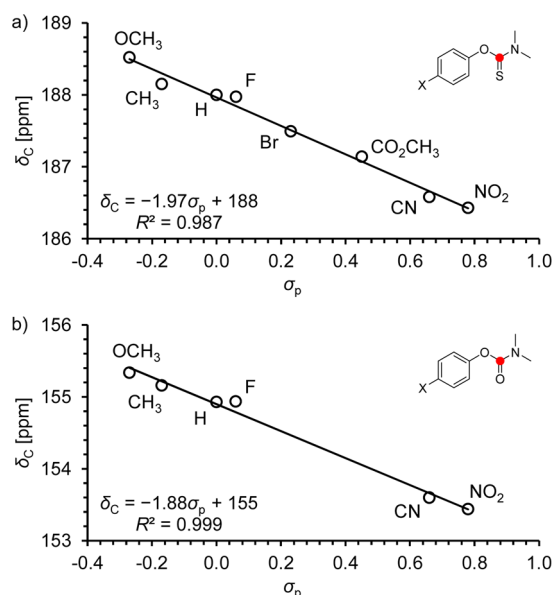


Figure 3. Hammett correlations found between the ^{13}C chemical shift values (δ_{C}) of the carbamate carbon atom and Hammett's constants of the substituents (σ_{p}) of the various O-aryl thiocarbamates (a) and O-aryl carbamates (b).¹⁸

at a higher field compared to both the thiocarbamates (~33 ppm) and selenocarbamates (~36 ppm). This corresponds well with the reported observation that the rotational barrier is reported to increase from amides through thioamides to selenoamides due to the decreased tendency for the atoms to participate in π -double bonds through the series $\text{O} > \text{S} > \text{Se}$.¹⁷ Plots of the ^{13}C resonances for the thiocarbamates and carbamates as a function of Hammett's σ_{p} constants linear correlations were generated for these also ($R^2 = 0.987$ and 0.999 ; Figure 3a and 3b), and together with the selenocarbamates **1** all three relationships were found to be practically parallel ($\rho = -1.93 \pm 0.05$).

The sensitivity to changes in electronic structure is reported to be about six times greater for the selenium resonances than for the carbon resonances on a similarly located carbon.¹⁹ The studied compounds do not let us make this direct comparison; however, there was still a clear trend that the electronic distribution at selenium is much more sensitive to changes in substituents than that at the adjoining carbon atom. This may be caused by the greater polarizability of selenium compared to carbon.²⁰ This trend also transpired in the linear free energy relationship that was found between the ^{77}Se chemical shifts and the ^{13}C chemical shifts of the selenocarbamate in compound **1** ($R^2 = 0.966$; Figure 2e). Here it was again shown how the ^{77}Se resonances follow the expected substituent chemical shift effect while the ^{13}C resonances obey the reverse effect since an increase in the shielding of the selenium resonance is accompanied by a

deshielding of the carbon resonance. This behavior is similar to the relationship reported for selenoketones and selenoamides.²¹

From the studied O-aryl selenocarbamates **1** and Se-aryl selenocarbamates **2** we were able to observe both one- and two-bond heteronuclear couplings between the ^{13}C – ^{77}Se nuclei. The $^1J_{\text{C-Se}}$ is also observed in the ^{13}C NMR spectrum in the form of symmetrically placed satellite signals surrounding the main peak, each having ~3.8% of the intensity of this peak (Figure 1b). The magnitude of the one-bond ^{13}C – ^{77}Se coupling constants ($^1J_{\text{C-Se}}$) between the carbamate carbon and the selenium atom in **1** was in the range of 236.5 Hz ($\text{X} = \text{OCH}_3$) to 241.6 Hz ($\text{X} = \text{NO}_2$). It has been reported that the Fermi contact interaction is the dominant mechanism influencing the $^1J_{\text{C-Se}}$ coupling.^{21,22} Consequently, the magnitude of the $^1J_{\text{C-Se}}$ coupling strongly depends on the hybridization of the carbon atom. While sp^3 hybridizations are leading to relatively small values of $^1J_{\text{C-Se}}$, an increase in s -character gives an increase in the magnitude. Ranges reported in the literature are 45–100 Hz for selenium attached to sp^3 carbon atoms, 90–174 Hz for sp^2 carbons in $\text{C}=\text{C}$ –Se systems containing partial double bond character while the coupling increases to 203–249 Hz for systems containing a true $\text{C}=\text{Se}$ bond.^{13,21} The high $^1J_{\text{C-Se}}$ values obtained from **1** therefore correspond well with the previous ones observed in the literature. By plotting the $^1J_{\text{C-Se}}$ values as a function of Hammett's σ_{p} constants, a linear regression was found ($R^2 = 0.986$; Figure 4a). The fact that we observe a linear free energy relationship between $^1J_{\text{C-Se}}$ and the σ_{p} constants is good evidence that the change in $^1J_{\text{C-Se}}$ results from electronic effect of the substituents. The magnitude of $^1J_{\text{C-Se}}$ is found to increase with the greater electron-withdrawing power of the substituents. This can be explained by looking at the lone pair electrons on the oxygen atom that will interact strongly with the aromatic ring when electron-withdrawing substituents are present. This interaction will weaken the delocalization toward the carbonyl carbon atom and thus give rise to an increase in the C–Se bond order and thereby a higher coupling constant.

Compound **2** retains two $^1J_{\text{C-Se}}$ couplings: one between the selenium atom and the *ipso* carbon and one to the carbamate carbon. Since the involved carbon atoms are both sp^2 hybridized, a lower coupling constant was therefore to be expected. The $^1J_{\text{C-Se}}$ couplings were measured in the ^{13}C NMR spectra to be between 92.6–123.6 Hz thereby confirming how the $^1J_{\text{C-Se}}$ coupling constant indeed depends on the hybridization. Besides the two $^1J_{\text{C-Se}}$ couplings, compound **2** also gives rise to a $^2J_{\text{C-Se}}$ coupling between the *ortho* carbon and the selenium atom. The two-bond ^{13}C – ^{77}Se coupling constant has a magnitude of 10.4–11.3 Hz showing how the coupling decreases as the distance between the two interacting nuclei increases. These values correspond nicely with previously reported $^2J_{\text{C-Se}}$ couplings that are shown to be in the range 5–30 Hz for various systems.^{22,23} Plotting both the $^1J_{\text{C-Se}}$ and $^2J_{\text{C-Se}}$ couplings in **2** as a function of Hammett's σ_{p} constants gave rise to linear correlations ($R^2 = 0.958$, 0.975 , and 0.934 ; Figure 4b, 4c, and 4d) indicating that the size of $^1J_{\text{C-Se}}$ correlates well with the electronic effects transmitted through the aromatic ring. The ρ value is negative in Figure 4b while it is positive in Figure 4c and 4d. The two latter show us therefore how electron-withdrawing substituents here increase the magnitude of $^1J_{\text{C-Se}}$ by increasing both the strength of the interaction of selenium with the aromatic

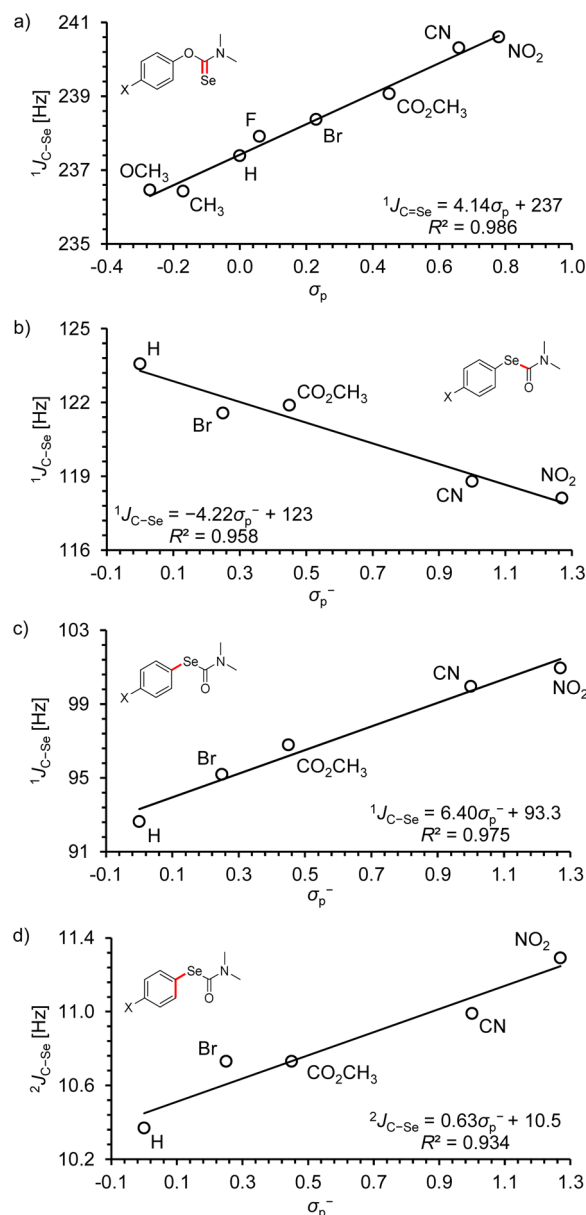


Figure 4. Hammett correlations found between the ^{13}C - ^{77}Se coupling constants ($^nJ_{\text{C-Se}}$) and Hammett substituent constants (σ_p or σ_p^-) of O-aryl selenocarbamates **1** (a) and Se-aryl selenocarbamates **2** (b-d).

ring and the $\text{C}_{\text{Ar}}\text{-Se}$ bond order whereas donating substituents decrease it. In general, the correlations for $^1J_{\text{C-Se}}$ show a greater numerical slope than that for the $^2J_{\text{C-Se}}$ coupling ($\rho = 4.1\text{--}6.4$ vs 0.6). This indicates that the substituent effects are transmitted most effectively through resonance rather than inductive effects.

No couplings were observed between the ^1H - ^{77}Se nuclei. In compound **1** the closest connection is a $^4J_{\text{H-Se}}$ coupling to the *N,N*-dimethylamino protons, but this is too weak to be observed. Compound **2** possesses a $^3J_{\text{H-Se}}$ coupling to the aromatic *ortho* protons. In general, 3J coupling constants are shown to exhibit a Karplus-type dependence where the size of the coupling constant depends directly on the torsional angle (α) between the atoms involved. The magnitude of the splitting is greatest when $\alpha = 0^\circ$ or 180° and is smallest when $\alpha = 90^\circ$.²⁴ The torsional angle, $^1\text{H-C}\equiv\text{C-Se}$, in a crystal

structure of **2** was measured to be ca. 3° .¹⁶ However, no $^3J_{\text{H-Se}}$ couplings were ever detected in the studied compounds, so it appears that any ^1H satellite signals were hidden under the main signal or too low intensity to be observed. Previous studies of $^3J_{\text{H-Se}}$ couplings in aromatic compounds estimate $^3J_{\text{H-Se}} \approx 3$ Hz.^{22,25}

CONCLUSION

In this paper we have presented the first systematic ^1H , ^{13}C , and ^{77}Se NMR spectroscopic study of a family of substituted O-aryl selenocarbamates **1** and Se-aryl selenocarbamates **2**, and we have showcased how the combination of ^{77}Se and ^{13}C NMR spectroscopy gives an internally consistent linear free energy relationship using Hammett substituent constants.

For compound **1** excellent linear free energy relationships ($\bar{R}^2 = 0.983$) were obtained when the NMR spectral parameters (δ_{X} and $^nJ_{\text{C-Se}}$) were plotted against Hammett's σ_p values while the correlation coefficients from the plots obtained with compound **2** were somewhat lower ($\bar{R}^2 = 0.888$). The substituents used in **1** represent both electron-withdrawing and -donating groups whereas in **2** they are only electron-withdrawing. While σ_p values are based on a combination of both resonance and polar interactions, Hammett's σ_p^- constants are optimized for compounds in which there is a direct resonance interaction between an electron acceptor and the studied site. It was therefore possible to obtain better plots when instead using Hammett's σ_p^- constants for the plots with **2** (one example with $R^2 = 0.702$; the rest $\bar{R}^2 = 0.957$).

In conclusion, the ^{13}C and ^{77}Se NMR spectra of O-aryl selenocarbamates **1** and Se-aryl selenocarbamates **2** have been analyzed and we were able to find linear correlations between selected ^{13}C and ^{77}Se chemical shift values and Hammett's σ_p and σ_p^- constants. Furthermore, we have determined both one- and two-bond heteronuclear couplings between the ^{77}Se - ^{13}C nuclei in **1** and **2** and shown how also these correlate with σ_p and σ_p^- .

EXPERIMENTAL SECTION

The synthesis of compounds **1** and **2** was reported in a previous study.¹⁶ The O-aryl thiocarbamates were synthesized following a literature procedure,²⁶ while the ^{13}C NMR spectroscopic data on the O-aryl carbamates were obtained from the literature.¹⁸

The samples for the NMR experiments were prepared using CDCl_3 as the solvent that was purchased from Euriso-Top and used as received. The concentration of the samples was in the range $0.10\text{--}0.20$ M (in general 20 mg of compound in 500 μL of CDCl_3). All NMR experiments were performed at 25°C . ^{13}C NMR spectra were recorded at 125 MHz on a 500 spectrometer equipped with a CryoProbe using residual nondeuterated CHCl_3 as the internal standard (δ_{C} 77.16 ppm). ^{13}C - ^{77}Se coupling constants ($^nJ_{\text{C-Se}}$) were obtained from the ^{77}Se satellites of the proton-decoupled ^{13}C NMR spectra. Due to the rather large longitudinal relaxation time of ^{77}Se the spectra were recorded with a longer relaxation delay ($T_1 = 4.0$ s) together with an extended number of scans ($n = 2048$) to minimize the signal-to-noise ratio and obtain the low intensity $^nJ_{\text{C-Se}}$. ^{77}Se NMR spectra were recorded at 57 MHz on a 300 spectrometer equipped with a 5 mm BBO probe using a saturated solution of diphenyl diselenide in CDCl_3 at 25°C in a sealed tube as an external standard (δ_{Se} 463 ppm). The experiments were performed with a relaxation delay of $T_1 = 2.0$ s and a prolonged number of scans ($n = 1024$). The spectra were recorded with a spectral width of 500 ppm, and to avoid any misinterpretation of potential aliased or folded peaks, each compound was recorded in at least two different spectral windows. All chemical shifts (δ) are quoted in ppm, and coupling

constants (J) are given as absolute values and expressed in hertz (Hz). The NMR experiments were processed using MestReNova v. 8.1.2.

■ ASSOCIATED CONTENT

■ Supporting Information

^{77}Se NMR spectra for compounds **1** and **2** together with tables containing the parameters used for the Hammett plots. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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