

Theoretical $^1\text{H}(\text{Se—H})$ NMR shifts in meta-substituted Ph—XH ($\text{X} = \text{O}, \text{S}, \text{Se}$)

Vladimir Sladek, Lenka Rottmannová, Peter Škorňa,
Michal Ilčin and Vladimír Lukeš

*Institute of Physical Chemistry and Chemical Physics, Slovak Technical University,
SK-81237 Bratislava, Slovakia
vladimir_sladek@stuba.sk*

Abstract: A systematic comparative theoretical study has been performed on a series of fourteen metasubstituted selenophenols. The optimal geometries were calculated using the density functional theory (DFT) and the Nuclear Magnetic Resonance parameters were computed by applying the Gauge Including Atomic Orbital (GIAO) method. The calculated NMR shifts were correlated with the Hammett constants. The obtained results were also compared with the theoretical data obtained for thiophenols and phenols. Our results indicate the linear dependence between the gas-phase NMR shifts and Hammett constants. However, the presence of large selenium atoms is able to suppress significantly the substituent effect in meta position. Therefore six substituents (Me, OH, MeCO, COOMe, COOEt and CF_3 groups) were excluded from the data evaluation. Correlations with the fundamental stretching vibration frequencies of the mode with the dominant Se—H vibration have not been found.

Keywords: chemical shift, NMR, Hammett constant, selenophenol, B3LYP

Introduction

The molecules containing the selenium atoms attract considerable attention during the last decades. The typical feature of these compounds is the toxicity and the particularly unpleasant smell. The toxicity is believed to originate in the ability of selenium to replace sulfur in proteins. Organoselenium compounds seem to be less toxic than salts which are readily soluble in water (Duddeck 1995). On the other hand, selenium is an essential trace element and some selenium-containing proteins, e.g. glutathione peroxidase, have been discovered. In several places of the world, selenium deficiency syndromes (e.g. Keshan disease) have been observed (Duddeck 1995). Medical treatments of heart diseases and of intoxications by arsenic, cadmium and mercury as well as cancer therapies and the stimulation of the immune system widely use selenium-containing substances (Newcomb et al. 1992). The inorganic selenium compounds, e.g. ZnSe, PbSe etc., play an important role as semiconductor materials for optoelectronic applications (Smith et al. 1993).

Among the “heavier” group 16 elements, selenium has been most widely studied by Nuclear Magnetic Resonance (NMR) spectroscopy, and this is now a rapidly developing field (Leeck et al. 1996). However, in many published works, the NMR parameters for selenium are hidden because the emphasis of these works was on a different topic. For example, some papers dealing with the reactivity of organoselenium compounds do not contain Se NMR spectra

but report Se—H or $^{77}\text{Se—}^{13}\text{C}$ coupling constants obtained from the H and ^{13}C NMR spectra, respectively. Other typical examples are works on the X-ray spectroscopy of selenium-containing metal complexes where ^{77}Se NMR data are given more or less as a by-product. The applications and biological relevance of ^{77}Se NMR spectroscopy is extensively discussed by (Duddeck et al. 1995) in detail. Here Me_2Se is reported as a common standard against which the chemical shifts are related.

Selenophenol and the substituted selenophenols are known among the most efficient radical traps and play a central role in the radical reaction rate measurements. Although much effort has been dedicated to the organoselenium NMR, there are few reports on the SeH proton shift of selenols. Proton NMR signals of some selenols were assigned at first by (Merijanien et al. 1969) as follows: at $\delta = 10.67$ ppm for ethaneselenol, at $\delta = 10.09$ ppm for *meta*-phenyl-selenophenol and at $\delta = 8.54$ ppm for selenophenol. Later, the selected number of para substituted aryl selenols were also studied by (Yan et al. 1995). They showed that the group attached to the selenium plays an important role in the chemical shift of the Se—H proton. Next, the linear correlation between the experimental $^1\text{H}(\text{Se—H})$ chemical shifts and Hammett (Hansch et al. 1991) constants for five para- and meta-substituted selenols was also reported by (Yan et al. 1995). The parameters of this dependency evaluated from this published data are

$$\log(\delta/\delta_0) = 0.1144\sigma_m - 0.0005 \quad (1)$$

Here δ and δ_0 are the chemical shifts (with respect to the tetramethylsilane) of the substituted and non-substituted system, respectively, and σ_m is the Hammett constant of the substituent.

Theoretical quantum chemical studies of π -conjugated systems can provide a fundamental understanding and considerable contribution in the design of novel molecules with targeted chemical or biological properties. Nowadays, the density functional theory (DFT) methods are applied successfully to the optimal geometry calculations and to the investigation of various physical properties, including the NMR spectra simulations. With respect to the above mentioned investigations, this study is focused on the theoretical investigations of NMR chemical shifts of selenophenols which are monosubstituted in *meta* positions with 14 electron-donating and electron-withdrawing groups. With respect to the approach of Yan et al. (1995) the chemical shifts will be correlated with the Hammett constants of the substituent groups as well as compared with the results obtained for the phenols and thiophenols.

Computational details

The singlet ground state structures of the studied molecules were optimized at the B3LYP/6-311++G** level of theory (i.e. the three parameter hybrid functional of Becke and Lee-Yang-Parr; Becke 1993). The used basis sets for Se are taken from (Binkley et al. 1980) and for the remaining atoms from

Gaussian03 basis set library (Frisch et al. 2003). The stability of all the optimized structures was checked by the vibrational analysis (no imaginary frequencies). The energy cut-off was of 10^{-4} kJ mol⁻¹ and the final root mean square energy gradient was under 0.005 kJ mol⁻¹ Å⁻¹. The numerical integration of the used functional was performed using the fine integration grid with default parameters. The NMR parameters were evaluated for the singlet ground state structure with the Gauge Including Atomic Orbital (GIAO) method (Ditchfield 1974). The ¹H chemical shifts are computed with respect to TMS (tetramethylsilane) and the ⁷⁷Se chemical shifts are related to Me₂Se (dimethylselenane). All the quantum chemical calculations were carried out using the Gaussian03 package (Frisch et al. 2003).

Results and discussion

The geometry optimization of the non-substituted selenophenols resulted in a planar structure. The average B3LYP C—C bond length in aromatic ring is of 1.394 Å and average C—H bond length is of 1.080 Å. The C—Se distance is of 1.931 Å and the Se—H distance is of 1.471 Å. The absolute value of the gas-phase B3LYP/GIAO/6-311++G** isotropic magnetic chemical shift for ⁷⁷Se in selenophenol is of 1556.177 ppm. The calculated chemical shift related to the Me₂Se (gas-phase B3LYP/GIAO/6-311++G**: 1621.245 ppm) is of 65.068 ppm. The absolute values of the gas-phase B3LYP/GIAO/6-

Tab. 1. The Hammett constant σ_m (Hansch 1991) for the meta position of the corresponding substituent and the B3LYP/GIAO/6-311++G** isotropic ¹H NMR shifts δ (X—H) (in ppm) in X—H groups, X = Se, S or O. The ¹H and ⁷⁷Se shifts are evaluated with respect to TMS. The ⁷⁷Se chemical shifts δ (Se) are related to Me₂Se (B3LYP/GIAO/6-311++G*: 1621.245 ppm). The vibration frequencies of the mode with dominant Se—H stretching vibration $\tilde{\nu}$ (Se—H) are in the last column.

Substituent	σ_m	δ (Se—H)	δ (S—H)	δ (O—H)	δ (Se)	$\tilde{\nu}$ (Se—H)/cm ⁻¹
H		3.763	3.675	3.742	65.068	2384
<i>m</i> -NH ₂	-0.16	3.542	3.464	3.511	79.682	2380
<i>m</i> -OiPr	0.10	3.699	3.560	3.655	70.492	2370
<i>m</i> -Br	0.39	3.817	3.700	3.830	93.049	2373
<i>m</i> -Cl	0.37	3.790	3.698	3.822	91.436	2388
<i>m</i> -CN	0.56	3.932	3.816	27.95	94.012	2389
<i>m</i> -COOEt	0.37	3.964	3.868	3.949	78.979	2373
<i>m</i> -COOMe	0.36	3.960	3.886	3.910	79.777	2376
<i>m</i> -Me	-0.07	3.815	3.607	3.673	52.975	2365
<i>m</i> -MeCO	0.38	4.057	3.929	3.981	81.689	2384
<i>m</i> -MeO	0.12	3.682	3.624	3.713	76.407	2382
<i>m</i> -OH	0.12	3.895	3.626	3.555	47.296	2358
<i>m</i> -SH	0.25	3.771	3.575	3.731	72.928	2372
<i>m</i> -F	0.34	3.819	3.730	3.869	92.402	2371
<i>m</i> -CF ₃	0.43	3.956	3.889	3.961	93.601	2376

311++G** isotropic chemical shift of ^1H for Se—H in selenophenol is of 1556.177 ppm.

The substitution at the aromatic ring has the direct influence on the chemical shifts of NMR active atoms. The calculated gas-phase B3LYP/GIAO/6-311++G** isotropic magnetic chemical shift (δ) for ^{77}Se and $^1\text{H}(\text{H—Se})$ atoms for 14 electron-donating and electron- withdrawing groups are collected in Table 1. For the sake of comparison, the ^1H chemical shifts for the phenols ($^1\text{H—O}$) and thiophenols ($^1\text{H—S}$) are also included. The optimized geometries of the latter molecules were taken from (Klein et al. 2006) and (Rimarčík et al. 2011). All chemical shifts are related to Me_2Se or TMS standards. The ^1H chemical shifts of $^1\text{H—X}$ groups are slightly lower for phenol (3.742 ppm) and thiophenol (3.675 ppm) than for the selenophenol (3.763 ppm).

The correlation of the theoretical chemical NMR shifts with the Hammett sigma parameters (Hansch, 1991) for meta substitution is possible only for the hydrogen ($^1\text{H—X}$). The correlation of ^{77}Se NMR shifts with the Hammett constants is not linear (correlation coefficient below 0.5). The data are given in Table 1.

We present chemical shifts with 3 decimal digits to avoid the implementation of round off errors. In Figures 1–3, according to (Yan et al. (1995)), the linearized logarithmic dependencies

$$\log \delta/\delta_0 = A \sigma_m + B \quad (2)$$

of the relative ^1H chemical shift of Se— ^1H and S— ^1H , O— ^1H and hydrogens with respect to the Hammett constants (σ_m) are depicted. The symbol δ_0 represents the NMR shift for the non-substituted molecule (i.e. phenol, thiophenol and selenophenol). In the case of the selenophenols, the linear regression (2) was obtained only for 8 data points with the correlation coefficient of 0.989, $A = 0.06 \pm 0.17$ and $B = -0.016 \pm 0.054$. The excluded substituents are depicted as open symbols (Me, Me-CO, COOMe, COOEt, CF_3 and OH groups). Although the obtained parameters are not identical with the experimental dependence obtained for the five para and meta analogues of selenophenols reported by (Yan et al. 1995), the qualitative trends agree. The main difference is caused probably by the inconsistent data, since Yan evaluated para substituted molecules as well.

An analogous linear dependence can be found for thiophenols and phenols. For thiophenols, the COOMe, COOEt, MeCO, CF_3 and Me are clearly out of the trend and the following linear regression (2) was evaluated for the remaining 9 substituents. The correlation coefficient is of 0.946, $A = 0.06 \pm 0.17$ and $B = -0.018 \pm 0.055$. Most of the substituents are in the linear correlation (2) for 12 meta substituted phenols with the correlation coefficient of 0.936. The parameters of the depicted linear dependence (see Fig. 3) with excluded OH and Me group can be expressed as $A = 0.09 \pm 0.16$ and $B = -0.018 \pm 0.055$.

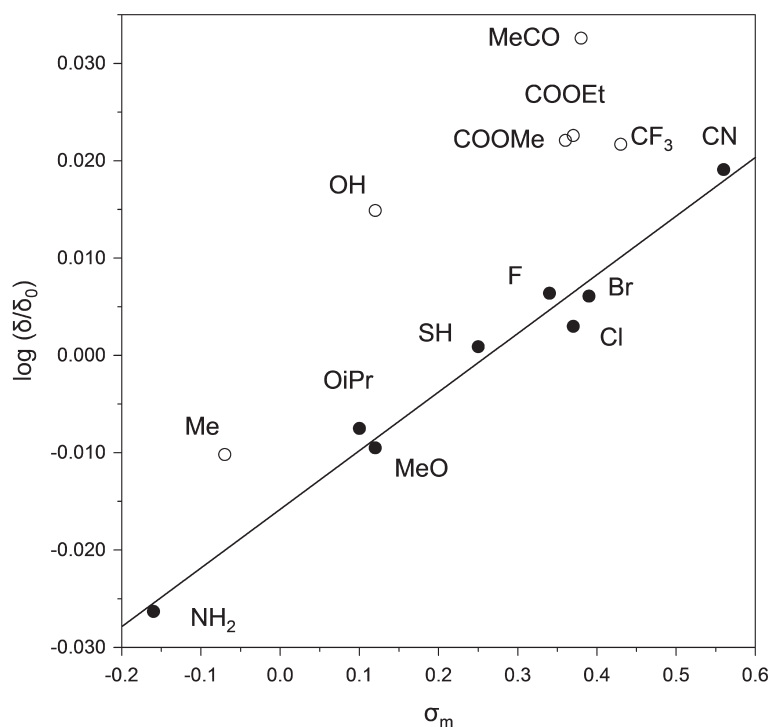


Fig. 1. The relationship between the Hammett constant and the ^1H chemical shift in Se— ^1H group with respect to TMS in meta-substituted selenophenols. The empty symbols are not included in the linear regression of Eq. (2).

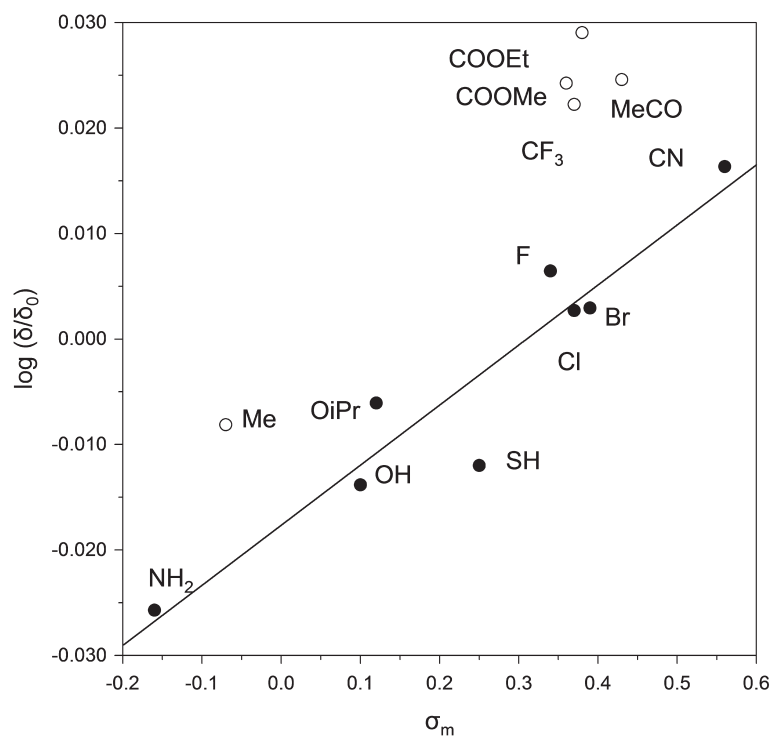


Fig. 2. The relationship between the Hammett constant and the ^1H chemical shift in $\text{S}-^1\text{H}$ group with respect to the TMS in meta-substituted thiophenols. The empty symbols are not included in the linear regression of Eq. (2).

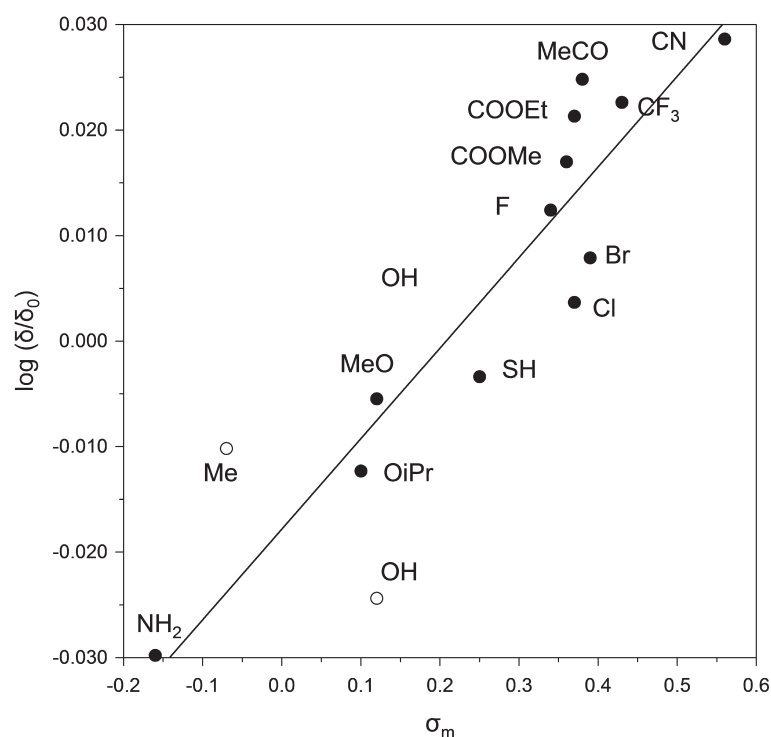


Fig. 3. The relationship between the Hammett constant and the ^1H chemical shift in $\text{O}-^1\text{H}$ group with respect to the TMS in meta-substituted phenols. The empty symbols are not included in the linear regression of Eq. (2).

The comparison of the above mentioned results indicate that the slope for the selenophenols is lower by about 0.0255 with respect to the phenols

and by 0.0034 higher than for thiophenols. Such comparison is however questionable, since more data points were excluded from the evaluation for

selenophenols than for phenols. It seems that the presence of large selenium (and sulphur) atoms is able to suppress the substituent effect in meta position.

The calculated frequencies of the fundamental Se—H stretching vibrations are listed in the last column of Table 1. The calculated gas-phase B3LYP value for the selenophenol is of 2384 cm⁻¹. This value is lower (by 83 cm⁻¹) than the experimental one (Lalezari and Sharghi 1964). Similar difference between the calculated gas-phase and available experimental value was obtained for the Me substituent. This fundamental vibration is at 2296 cm⁻¹ whereas we calculated a value of 2365 cm⁻¹. In both cases we meet with the experimental values within 3 %. The correlation of the Se—H fundamental vibration of meta substituted selenophenols with the Hammett constants is not relevant (correlation coefficient below 0.7). Similar result based on experimental data was also reported by (Yan et al. 1995) for the para substituted selenophenols.

Conclusions

In this work, we have performed the systematic comparative theoretical study on a series of fourteen monosubstituted selenophenols in meta position. The calculated gas phase proton NMR shifts were correlated with the Hammett constants. The obtained results were also compared with the theoretical data obtained for the thiophenols and phenols. Our results indicate the linearity between the gas-phase NMR shifts and Hammett constants. However, the presence of large selenium atoms is able to suppress significantly the substituent effect in the meta position. Therefore six groups were excluded from the data evaluation. Maybe the validity of the use of Hammett constants for selenols (selenophenols) has to be reevaluated. The correlations of the fundamental harmonic gas-phase stretching vibration frequencies of the mode with the dominant Se—H vibration were not found.

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