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Stereochemical study of the sterically crowded phenylselanylalkenes by means of ^{77}Se–^{1}H spin–spin coupling constants

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Stereochemical study of five sterically crowded phenylselanylalkenes obtained via the hydroselenation of either terminal or internal alkynes with benzeneselenol catalyzed by the nanosized Ni complexes has been carried out based on the experimental HMBC measurements and theoretical second order palarization propagator approach (SOPPA) calculations of their ^{77}Se–^{1}H spin–spin coupling constants across double bond in combination with the energy-based theoretical conformational analysis performed at the MP2/6-311G level. It has been found that studied phenylselanylalkenes adopt mainly skewed *s-cis* conformation with the noticeable out-of-plane deviations of the phenylselanyl and phenyl groups. Copyright © 2011 John Wiley & Sons, Ltd.**

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Introduction

Functionalized selanylalkenes, providing a wide spectra of their application in material science, organic synthesis and being the potential precursors of the selenium-based biologically active molecules,[1,2] have now become accessible through the recently developed regio- and stereoselective addition of selenoles to alkynes catalyzed by the nanosized Pd and Ni particles stabilized with organic sulfur or selenium ligands.[3] Apart from their practical application, polyfunctionalized selanylalkenes demonstrate an interesting conformational behavior due to the marked steric effects in the sterically crowded olefinic moiety which is the main subject of the present communication studied using ^{77}Se–^{1}H spin–spin coupling constants across double bond. Considered herewith are five most typical representatives of this series, compounds **1–5** (Scheme 1), obtained via heterogeneous Ni-based catalytic regioselective hydroselenation of terminal alkynes (to give compounds **1–3**) and stereoselective hydroselenation of internal alkynes (to give compounds **4** and **5**), as described elsewhere[3b].

Based on our previous results on the marked stereospecificity of geminal and vicinal J(Se,H) couplings in respect with the mutual orientation of the selenium lone pair and the corresponding coupling pathway in divinyl selenide,[4] selenophenes,[5] selenosugars [6] and selenium-containing heterocycles,[7] in this communication we employ vicinal selenium–proton couplings across double bond measured experimentally and calculated theoretically for the stereochemical study of **1–5** dealing with the internal rotation around the Se–C bonds. These results are supplemented with the energy-based theoretical conformational analysis performed at the MP2/6-311G** level.

Results and Discussion

Collected in Table 1 are the experimental values of *transoidal*, $^{3}J(\text{Se,H}_A)$, and *cisoidal*, $^{3}J(\text{Se,H}_B)$, vicinal selenium–proton couplings measured in the ^{77}Se–^{1}H HMBC spectra of **1–5**, as exemplified for compound **3** in Fig. 1. It is noteworthy that *transoidal* couplings across double bond (*ca.* 7–8 Hz) are somewhat larger than *cisoidal* ones (*ca.* 4–5 Hz) in this series, being in line with our previous findings in divinyl selenide[4] and selenium-containing heterocycles.[7] The only exception is compound **4** with *cisoidal* coupling $^{3}J(\text{Se,H}_B) = 10$ Hz, at least twice as large as in the rest of compounds under study, being even larger than the *transoidal* couplings in this series. On the other hand, the absolute value of the difference between $^{3}J(\text{Se,H}_A)$ and $^{3}J(\text{Se,H}_B)$ is pretty moderate (only *ca.* 3–4 Hz), and these two unexpected facts are the subject of a more detailed discussion given below based on the theoretical calculation of the model dihedral angle dependences of $^{3}J(\text{Se,H}_A)$ and $^{3}J(\text{Se,H}_B)$ shown in Fig. 2.

All calculations of J(Se,H) were performed at the Second order polarization propagator approach, SOPPA,[8] taking into account all four non-relativistic coupling contributions to the total coupling, namely, Fermi contact, J_{FC}, spin-dipolar, J_{SD}, diamagnetic spin–orbital J_{DSO}, and paramagnetic spin–orbital, J_{PSO}, terms. For selenium, we used Dunning's correlation-consistent triple zeta basis set, cc-pVTZ,[9] with decontracted *s*-functions and augmented with two tight *s*-functions ($\xi_1 = 63865962.54$ and $\xi_2 = 426498512.2$) referred to as cc-pVTZ-su2, as reported recently by some of us.[5b] Sauer's contracted aug-cc-pVTZ-J basis set[10] was employed for the hydrogens involved in the spin–spin coupling

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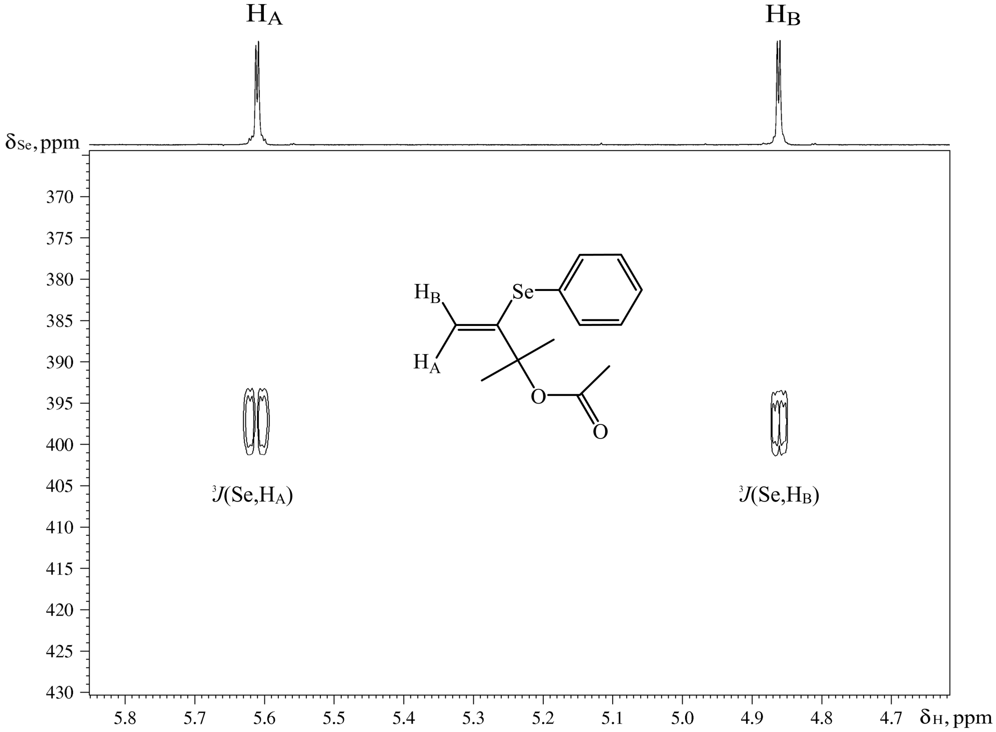
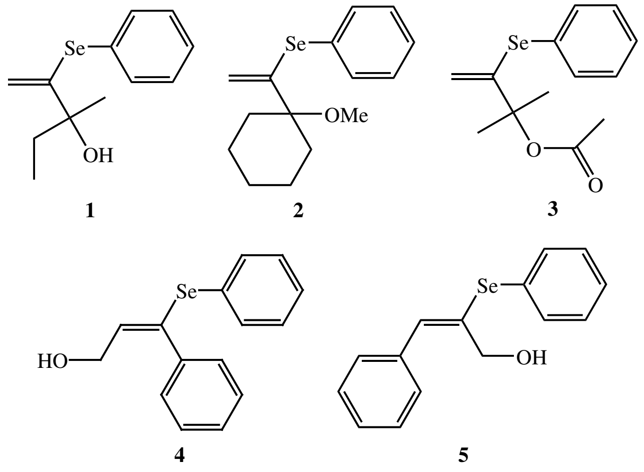


Figure 1. The olefinic region of the ^{77}Se$-^{1}$H HMBC spectrum of 2-methyl-3-(phenylselanyl)but-3-en-2-yl acetate (**3**) in $CDCl_3$ (^{1}H, 400.13 MHz; ^{77}Se, 76.34 MHz).



Scheme 1. Numeration of phenylselanylalkenes.

with selenium while standard Dunning's cc-pVDZ basis set[9] was used for all uncoupled atoms.

Fermi contact term was found to be dominant in all cases with the overall contribution of the non-contact terms being almost next to negligible in most cases. Out of the three non-contact terms, J_{SD}, J_{DSO} and J_{PSO}, only paramagnetic spin–orbital contribution, J_{PSO}, is of any practical significance, and this is exemplified by the data presented in Table 2 for a model selanylalkene.

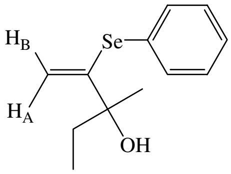
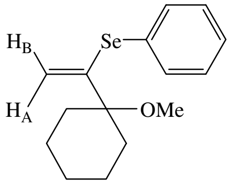
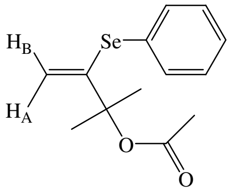
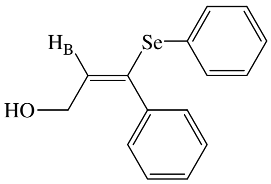
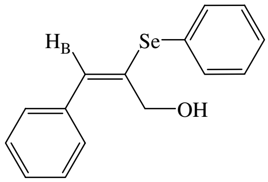
Coming back to the dihedral angle dependences of ^{3}J(Se,H$_A$) and ^{3}J(Se,H$_B$) calculated for the same model selanylalkene and shown in Fig. 2, it is evident that the difference between *cisoidal* and *transoidal* couplings is strongly affected by the value of the dihedral angle itself, the former falling into the range of *ca.* 4–5 Hz for $\varphi = 0$–$60°$ to *ca.* 15–20 Hz for $\varphi = 120$–$180°$ with the *transoidal* coupling being larger in the whole range of $\varphi = 0$–$180°$. Now it becomes clear why experimental *cisoidal* ^{3}J(Se,H$_B$) and especially *transoidal* ^{3}J(Se,H$_A$) are so small and why experimental difference of those couplings does not exceed 3–4 Hz in most cases.

The answer lies in the very fact that the preferable conformations in this series are skewed *s-cis* (which corresponds to the range of $\varphi = 0$–$60°$). Indeed, in this range of φ the value of ^{3}J(Se,H$_A$) is markedly decreased due to the diminished selenium lone pair effect in the *cisoidal* conformation resulting in the unusually small difference of ^{3}J(Se,H$_A$) and ^{3}J(Se,H$_B$) mentioned above.

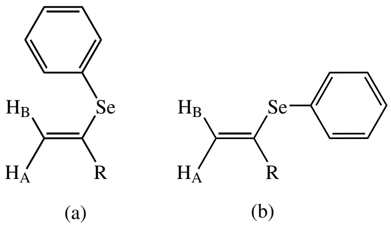
To support this finding based on the experimental and calculated ^{77}Se$-^{1}$H couplings, we have carried out the energy-based theoretical conformational analysis of **1–5** performed at the MP2/6-311G** level. For each of the five compounds under scrutiny, two true-minimum conformers, skewed *s-cis* (*A*) and skewed *s-trans* (*B*) were localized, as schematically depicted in Scheme 2. All localized true-minimum conformers of **1–5** are shown in Figs. 3 and 4 while the results of the performed theoretical conformational analysis adopting Boltzmann distribution of conformations are collected in Table 3.

The skewed *s-cis* conformer dominates for compounds **1–3** and **5** (92–98%) while selanylalkene **4** exists mainly in the form of the skewed *s-trans* conformation *B* (73%). This is the answer on why ^{3}J(Se,H$_B$) = 10 Hz in **4** is so large as compared to that in the rest of compounds in this series (4–5 Hz), see Table 1. Indeed, due to the dihedral angle dependence of ^{3}J(Se,H$_B$) shown in Fig. 2, the value of this coupling should actually be around 10–12 Hz for the *s-trans* conformer with the dihedral angle φ falling into range of 120–150°.

Table 1. Experimental values of ^3J(Se,H$_A$) and ^3J(Se,H$_B$) in the series of **1–5**

Compound	Notation of atoms	^3J(Se,H$_A$)	^3J(Se,H$_B$)
1		7.4	4.7
2		7.2	4.0
3		8.4	4.3
4			10.0
5			5.2

CDCl$_3$, 25 °C; All couplings are in Hertz.



Scheme 2. True-minimum conformers, skewed *s-cis* (a) and skewed *s-trans* (b), of phenylselanylalkenes **1–5**.

Another interesting question is why the preferable conformation of selanylalkene **4** is *s-trans* in contrast to the rest of selanylalkenes **1–3** and **5** existing in the form of the predominant *s-cis* conformer, see Table 3. The most reasonable explanation of this fact is the favorable π-stacking of two phenyl rings oriented in a 'stack of coins' fashion in the *s-trans* conformation of **4**, as can be seen in Fig. 4. The stabilizing effect of aromatic π-stacking is well known[11] and has received a good deal of theoretical interest[12].

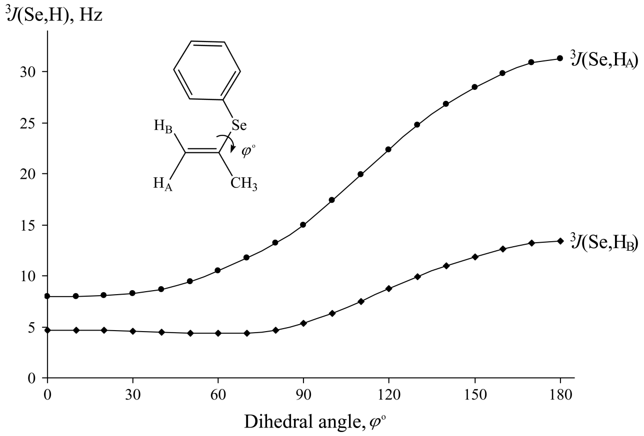


Figure 2. Dihedral angle dependences of ^3J(Se,H$_A$) and ^3J(Se,H$_B$) calculated in the model phenylselanylalkene at the SOPPA level. The value of $\varphi = 0°$ is assigned to the ideal *s-cis* conformation, as shown.

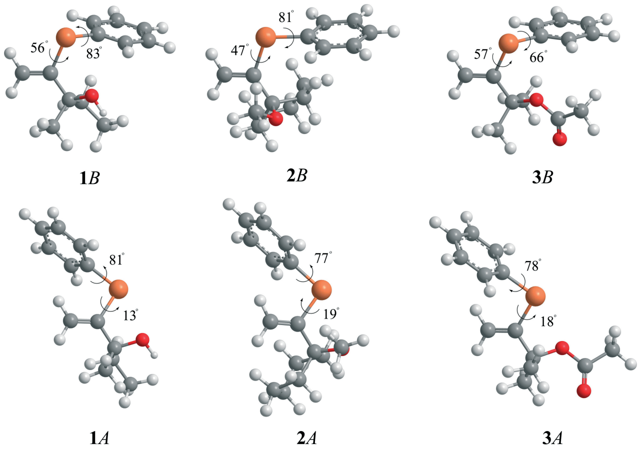


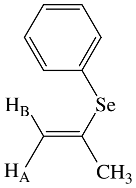
Figure 3. Equilibrium structures of the localized true-minimum conformers of **1–3** optimized at the MP2/6-311G** level. Element colors: selenium – brown, oxygen – red, carbon – gray; hydrogen – light gray. Shown on structures are the out-of-plane deviations of the phenylselanyl and phenyl groups in respect with the rotation around the Se–C bonds.

As follows from the data presented in Figs. 3 and 4, both true-minimum conformers, *A* and *B*, in the whole series of **1–5** show marked out-of-plane deviations in respect with the rotation around both Se–C bonds which is due to the strong steric effects involving the phenyl ring of the phenylselanyl group and substituted olefinic moiety in both conformations of **1–5**.

Concluding Remarks

The main conclusion drawn from the present results deals with the practical utilization of vicinal ^{77}Se–^{1}H couplings across double bond for a configurational assignment of selanylalkenes. It follows that experimental measurements of ^3J(Se,H) should be supplemented with a detailed theoretical study to avoid erroneous configurational assignment at the double bond of unsaturated organoselenium compounds (as can be mistakenly done, e.g., for compound **4**, provided only experimental value of ^3J(Se,H) was used for this purpose). Traditional Karplus-type dihedral angle dependence of ^3J(Se,H) may be heavily affected by the orientation of the terminal substituent bearing selenium atom, as was found

Table 2. Individual coupling contributions to spin–spin coupling constants ^3J(Se,H) across double bond in a model selenoalkene calculated at the SOPPA level

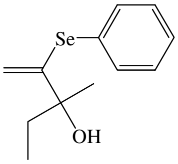
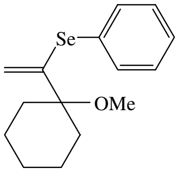
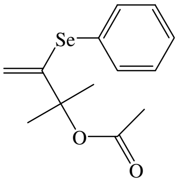
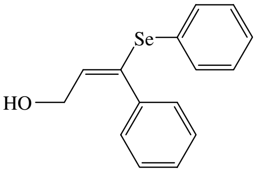
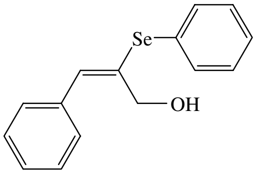


Spin–spin coupling constant	J_{DSO}	J_{PSO}	J_{SD}	J_{FC}	J_{calc}	J_{exp}[a]
^3J(Se,H$_A$)	−0.26	−0.81	0.07	9.27	8.27	7.4
^3J(Se,H$_B$)	0.04	−0.66	−0.25	5.44	4.57	4.7

Preferable skewed *s-cis* conformation is adopted as shown schematically in the table. All couplings and coupling contributions are in Hertz.

[a] Measured in compound **1**, this work.

Table 3. MP2/6-311G** theoretical energy-based conformational analysis of **1–5**

Compound	Structure	Conformer	Relative energy (kJ/mol)	Population (%)[a]
1		*A*	0.0	98
		B	9.5	2
2		*A*	0.0	99
		B	15.8	1
3		*A*	0.0	97
		B	9.0	3
4		*A*	2.5	27
		B	0.0	73
5		*A*	0.0	92
		B	6.0	8

[a] Derived from the relative energies of the individual conformers adopting Boltzmann distribution of conformations.

here in the series of sterically crowded phenylselanylalkenes. Based on the combined theoretical and experimental study of the vicinal selenium–proton coupling constants across double bond, the compounds under scrutiny were shown to adopt mainly skewed *s-cis* conformation (except the one with a strong π-stacking stabilization of *s-trans* conformer) with the noticeable out-of-plane deviations of the phenylselanyl and phenyl groups due to the marked steric effects.

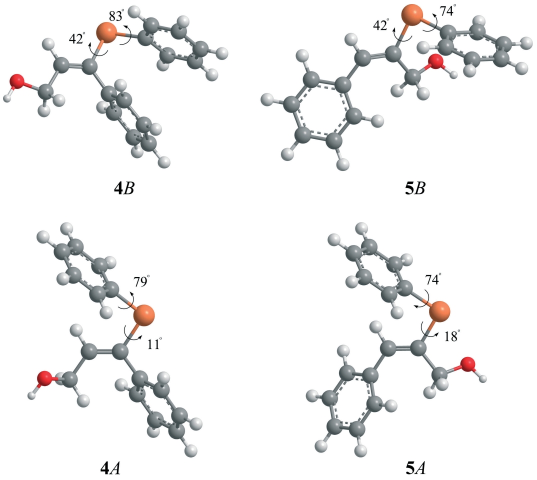


Figure 4. Equilibrium structures of the localized true-minimum conformers of **4** and **5** optimized at the MP2/6-311G** level. Element colors: selenium – brown, oxygen – red, carbon – gray; hydrogen – light gray. Shown on structures are the out-of-plane deviations of the phenylselanyl and phenyl groups in respect with the rotation around the Se–C bonds.

Experimental

NMR Measurements

^{1}H,^{13}C and ^{77}Se NMR spectra were recorded on a Bruker AVANCE-400 spectrometer (^{1}H, 400.13 MHz; ^{13}C, 100.62 MHz; ^{77}Se, 76.34 MHz) in a 5 mm broadband probe at 25 °C in $CDCl_3$ with hexamethyldisiloxane (^{1}H,^{13}C) and dimethylselenide (^{77}Se) as internal standards. Experimental measurements of ^{77}Se–^{1}H spin–spin coupling constants were carried out from the ^{77}Se–^{1}H HMBC spectra recorded using spectral windows of 3490 Hz with 2 K data points for ^{1}H, and 9540 Hz with 128 increments for ^{77}Se and 8 scans for each increment, resulting in the total experiment time of 60 min for each sample.

Computational Details

Localization of stationary points and geometry optimizations of **1**–**5** were performed with the GAMESS code[13] at the MP2/6-311G** level without symmetry constraints. All calculations of spin-spin coupling constants have been carried out taking into account all four non-relativistic coupling contributions with the DALTON package[14] at the SOPPA level using the stationary equilibrium MP2/6-311G** geometries.

General Synthetic Part

Ni(acac)$_2$ was dried in vacuum (0.01–0.02 Torr, 60 °C, 30 min) before use. Solvents were purified according to published methods. Products were purified by dry column flash chromatography.[15] The isolated yields given below were calculated based on initial amount of the alkyne. Nanosized Ni catalyst was prepared *in situ* from Ni(acac)$_2$ during the synthetic procedure as described earlier.[3b]

Synthetic Procedure (1–5)

Alkyne (1.0×10^{-3} mol) was added to Ni(acac)$_2$ (2.0×10^{-5} mol) and stirred at room temperature until uniform green suspension was formed (*ca.* 2–5 min). PhSeH (1.2×10^{-3} mol) was added to the stirred mixture at *ca.* 5 °C (water/ice bath). The stirring was continued for additional 10 min and the color of the suspension changed from green to dark. The reaction was stirred 1.5 h at 20 °C for **1** and 2–4 h at 60 °C for **2**–**5** (complete conversion of the alkyne was checked by NMR monitoring).

After completion of the reaction the products were purified by flash chromatography on silica with hexane/ethylacetate gradient elution. After drying in vacuum the pure products were obtained with the yields: **1** – 74%, **2** – 88%, **3** – 85%, **4** – 29%, **5** – 62%. All products were identified according to the published NMR data.[3b]

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