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Structural trends of ⁷⁷Se-¹H spin-spin coupling constants and conformational behavior of 2-substituted selenophenes

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Experimental measurements and second-order polarization propagator approach (SOPPA) calculations of ⁷⁷Se-¹H spin-spin coupling constants together with theoretical energy-based conformational analysis in the series of 2-substituted selenophenes have been carried out. A new basis set optimized for the calculation of ⁷⁷Se-¹H spin-spin coupling constants has been introduced by extending the aug-cc-pVTZ-J basis for selenium. Most of the spin-spin coupling constants under study, especially vicinal ⁷⁷Se-¹H couplings, demonstrated a remarkable stereochemical behavior with respect to the internal rotation of the substituent in the 2-position of the selenophene ring, which is of major importance in the stereochemical studies of the related organoselenium compounds. Copyright © 2009 John Wiley & Sons, Ltd.

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Introduction

In continuation of our previous study of the stereochemical behavior of 77 Se $^{-1}$ H spin-spin coupling constants in divinyl selenide,^[1] in the present communication, we report the results of the combined theoretical and experimental study of their structural trends in the series of selenophene (1) and its 2-substituted derivatives **2**–**7**, the recognized starting materials for many organoselenium syntheses.^[2]



This paper has specially focused on the computational aspect of ⁷⁷Se-¹H spin-spin coupling constants, which is of major importance in view of the very limited amount of the corresponding data obtained at high level of the modern ab initio theory. In our first publication,^[1] it has been established that vicinal and geminal ⁷⁷Se-¹H spin-spin coupling constants across or adjacent to double bond show a very strong stereochemical behavior with respect to the spatial orientation of the selenium lone pair; for example, a dramatic orientational effect of the selenium lone pair on geminal 77 Se $^{-1}$ H coupling (*ca* 60 Hz) was found in divinyl selenide, which makes these couplings to be of major importance in the conformational analysis of organoselenium compounds. Apart from our current interest in the structural trends and computational aspects of ⁷⁷Se-¹H spin-spin coupling constants, the goal of the present study was also to examine the conformational behavior of 2-substituted selenophenes with respect to the internal rotation of the substituent in the 2-position of the selenophene ring.

Results and Discussion

In accord with the main goal of the present investigation, first of all we have performed the benchmarked calculations of two possible 77 Se $^{-1}$ H spin $^{-}$ spin coupling constants, namely geminal, 2 J(Se,H-2), and vicinal, 3 J(Se,H-3), ones in the conformationally rigid (and thus ideally suitable for this purpose) selenophene (1) at different levels of theory with a variety of basis sets.

Three different methods have been used, namely, SOPPA^[3–5] (second-order polarization propagator approach), SOPPA(CCSD)^[6] providing a combination of the classical SOPPA with CCSD (coupled cluster singles and doubles) and also DFT-B3LYP, giving the most popular combination of the Becke three-parameter hybrid functional^[7] with the Lee, Yang and Parr functional.^[8] We have deliberately not used the uncorrelated HF-SCF level, even for evaluation of the electron correlation effects in the calculations of ⁷⁷Se⁻¹H couplings within the framework of the wavefunction methods SOPPA and SOPPA(CCSD), which are definitely of crucial importance and should necessarily be taken into account. The choice of these methods was determined by their well-known high performance and popularity in calculations of different types of spin–spin couplings documented in a number of publications (for reviews, see Ref. [9]).

On the other hand, six different basis sets were used for the coupled atoms: three standard correlation-consistent bases

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of Dunning,^[10] namely, cc-pVXZ (X = D, T) and aug-cc-pVTZ, together with the former two with decontracted s-functions and augmented with two tight s-functions ($\xi_1 = 63865962.54$ and $\xi_2 = 426498512.2$ for selenium), cc-pVXZ-su2 (X = D, T) and also the basis set aug-cc-pVTZ-J originally proposed by Enevoldsen, Oddershede and Sauer^[6] for calculation of spin-spin coupling constants and extended in the present paper for selenium. The rest of the atoms (uncoupled) were specified with Dunning's cc-pVDZ in all the cases.

It is well known that standard energy optimized basis sets are in general not flexible enough to represent the operators involved in the calculation of indirect nuclear spin-spin coupling constants correctly.[11-14] Consequently, several attempts have recently been made to develop basis sets suitable for highaccuracy calculations of spin-spin coupling constants.[6,15-22] They are all modifications of standard basis sets and are based on the fact that the Fermi contact (FC) operator contains a delta function and measures the electron density at the position of the nucleus and that standard basis sets do not give a good description of this part of the wavefunction. In the basis sets by Jensen and coworkers,^[21,22] tight p- and d-type functions are also added in order to give a better description of the paramagnetic spin orbit (PSO) and spin-dipolar (SD) terms for the cases where these contributions are of the same order of magnitude as that of the FC term. However, this is not the case for any of the ⁷⁷Se-¹H spin-spin coupling constants investigated here; therefore, we concentrate only on the FC term.

One of these optimized basis sets is called 'aug-cc-pVTZ-J'^[6,15,16] and is based on the correlation consistent aug-cc-pVTZ basis sets by Dunning and coworkers.^[10] The original basis sets were then modified in three ways: (i) The contraction of all basis functions was completely removed. (ii) Four s-type functions with very large exponents were added in the case of all atoms and three sets of d-type functions with large exponents were added to the third row atoms Al, Si, P, S and Cl. The exponents of the additional functions were obtained in an even-tempered fashion from the ratio between the two largest exponents in the original basis set. (iii) The additional 'aug' diffuse second polarization function (d-type for H and f-type for all other atoms) was removed. The resulting basis sets, called 'aug-cc-pVTZ-Juc',^[15] are rather large. In order to reduce the size, one could either employ a locally dense basis set scheme^[23] or recontract the basis set again. Geertsen^[14] or Guilleme and San Fabián^[18] have e.g. recontracted their basis sets with the SCF molecular orbital coefficients of the molecule in question. However, this would require a basis set optimization for each new molecule studied, which is rather inconvenient. In the aug-cc-pVTZ-J basis sets, this idea was therefore generalized and the SCF molecular orbital coefficients of the simplest hydride of each atom in question were used as contraction coefficients.^[15,16] The aug-cc-pVTZ-J basis sets were originally developed for correlated wavefunction calculations at the level of the SOPPA or SOPPA(CCDS) method,^[4,5,6] but were afterward also shown to perform very well in density functional theory (DFT) calculations,^[19,24] e.g. in comparison with a much larger basis set based on the correlation consistent cc-pCV5Z basis set.^[19]

However, an aug-cc-pVTZ-J basis set for selenium has so far not been published. Following the scheme described above, we have therefore generated a corresponding basis set for Se. All the calculations during the basis set optimization were performed on H₂ Se and at the SOPPA level. For hydrogen, the aug-ccpVTZ-J basis set was employed in all the steps. For Se, we started with the aug-cc-pVTZ basis set by Wilson et al.[25] and

removed the contraction completely. Stepwise addition of up to four additional tight s-type functions with exponents obtained as even-tempered series from the ratio (6.678025278) between the two largest s-type functions in the original basis set showed that convergence is already obtained with two additional s-type functions with exponents 63865962.54 and 426498512.2. Addition of up to three tight p-type or four tight d-type functions with exponents obtained analog to the s-type functions did not change the result any further. The final uncontracted basis set therefore consisted of 23 sets of s-type, 14 sets of p-type, 10 sets of d-type and 2 sets of f-type functions (23s14p10d2f). Using the molecular orbital coefficients of H₂ Se in this basis set, it was contracted to [12s9p6d2f] in a 14-14-14-1-1-1-1-1-1-1-1/13-13-13-1-1-1-1-1-1/8-1-1-1-1/1-1 scheme. The final basis set aug-cc-pVTZ-J for selenium is given in Table 1.

For fourth row atoms like Se, one can expect that relativistic effects play some role (for reviews, see Ref. [26]). A fully relativistic theory of spin-spin coupling constants, i.e. based on the Dirac equation, has already been presented some time ago,^[27] but the number of applications is still very small and, more important, no implementation based on correlated wavefunction methods as used in the present work is yet available apart from a recent fourcomponent Dirac-Kohn-Sham implementation.^[28] Relativistic and electron correlation effects are, however, not additive,^[29] and calculations of spin-spin coupling constants at the uncorrelated HF-SCF level are often qualitatively wrong. The predictive power of the recent Dirac-Hartree-Fock calculation of the one-bond Se-H coupling in H₂ Se^[30] is therefore uncertain. Alternatively, one can include relativistic effects also via perturbation theory or twocomponent approaches.^[26,31,32] Recent correlated calculations of this type on H₂ Se or GeH₄^[32] indicate the relativistic corrections to one-bond X-H couplings for atoms X, like Ge or Se, are in the order of 10%.

In a comparison with experimental coupling constants measured in liquids, one should also consider the effect of nuclear motion, i.e. vibrational corrections, and the solvent shift. Although vibrational corrections of one-bond X-H coupling constants can amount up to 5%,^[33] for two- or three-bond couplings, they are typically less than 1 Hz as shown in recent calculations on Pyrrole, Furan and Thiophene.^[34] Similarly, it is known that the solvent shifts for two- or three-bond couplings are typically very small.^[35]

Results of the benchmark calculations of ²J(Se,H-2) and ³J(Se,H-3) in selenophene (1) carried out at different levels of theory taking into account all four coupling contributions to the total coupling, J: Fermi contact, J_{FC}, spin-dipolar, J_{SD}, diamagnetic spinorbital, J_{DSO}, and paramagnetic spin-orbital, J_{PSO}, are compiled in Table 2. It follows that generally the wavefunction methods SOPPA and SOPPA(CCSD) perform much better as compared to the density functional method DFT-B3LYP for both couplings. This is especially obvious in the case of geminal ⁷⁷Se-¹H coupling, which is essentially overestimated within the DFT framework. On the other hand, computationally more demanding SOPPA(CCSD) does not show any noticeable advantages as compared to the parent SOPPA method. Among six basis sets under consideration, contracted Sauer's aug-cc-pVTZ-J and decontracted Dunning's cc-pVTZ-su2 with two tight s-functions are apparently the best. Keeping this in mind, we performed our further calculations of all ⁷⁷Se⁻¹H coupling constants in the whole series of 2-substituted selenophenes 1-7 at the SOPPA level with two most efficient basis sets, namely, aug-cc-pVTZ-J (Table 3) and cc-pVTZ-su2 (Table 4).

Before discussing these data, it should be noted that, in contrast to compounds 1-3 possessing no rotational conformers,

Table 1.	Exponents and contraction coefficients in the aug-cc-pVTZ-J basis set for Se (23s14p10d2f) \rightarrow [12s9p6d2f]												
Туре	Exponents			Contra	iction co	efficier	nts						
s	426498512.2	0.5545D-07	-0.1736D-07	0.6831D-08									
	63865962.54	0.4397D-06	-0.1375D-06	0.5409D-07									
	9563600.0	0.5798D-05	-0.1815D-05	0.7142D-06									
	1432100.0	0.04938	-0.01544	0.6075D-05									
	325910.0	0.02568	-0.08046	0.03166									
	92312.0	0.01086	-0.03401	0.01337									
	30116.0	0.03939	-0.01239	0.04881									
	10872.0	0.01270	-0.04017	0.01581									
	4240.1	0.03671	-0.01186	0.04690									
	1/58.4	0.09386	-0.03153	0.01250									
	766.59	0.2017	-0.0/464	0.03002									
	348.43	0.3280	-0.1452	0.05972									
	164.03	0.3238	-0.2038	0.08841									
	79.142	0.1352	-0.07887	0.03045	1								
	55.524				1.	1							
	17.505					1.	1						
	3 7405						1.	1					
	1 6890							1.	1				
	0 50927									1			
	0.25520										1.		
	0.10651											1.	
	0.039201												1.
р	8004.3	0.00045050	-0.00017830	0.00004300									
	1896.9	0.00390490	-0.00155540	0.00037700									
	614.71	0.02109010	-0.00847270	0.00204650									
	233.50	0.08129200	-0.03362450	0.00818990									
	97.856	0.22178410	-0.09582670	0.02333560									
	43.514	0.39072700	-0.18139070	0.04498130									
	20.063	0.35597140	-0.15031520	0.03574750									
	9.1127	0.10732720	0.19482630	-0.05868660	1.								
	4.1063	0.00369850	0.54155540	-0.17095730		1.							
	1.79490	0.00180320	0.38372990	-0.12935830			1.						
	0.62432	-0.00045010	0.04442320	0.26470630				1.					
	0.24615	0.00022080	-0.00501320	0.57780690					1				
	0.088917	-0.00007220	0.00168790	0.32755080					١.	1.			
d	261.05	0.00156550											
u	108 55	0.001333630											
	A1 A33	0.01332020											
	17 579	0.00013270											
	7 8627	0.31956900											
	3,5180	0.38120290	1.										
	1.5348	0.27460860		1.									
	0.60813	0.07825510			1.								
	0.22200					1.							
	0.08370						1.						
f	0.462	1											
	0.188		1.										
	51100												

2-substituted selenophenes **4–7** exist in the equilibrium mixture of two rotamers, *s-cis* and *s-trans*, due to the internal rotation around the C²–X bond. Therefore, all calculated values of J(Se,H) in the series of **4–7** given in Tables 3 and 4 were conformationally averaged in accord with the results of theoretical energy-based conformational analysis of **4–7** performed at the MP2/6-311G^{**}

level and based on the rotational potential energy curves and probability density of population distributions obtained as described in our recent publications.^[1,36] Refined search of stationary points in the areas of two minima ($\varphi \approx 0$ and 180°) and one maximum ($\varphi \approx 90^{\circ}$) of **4–7** resulted in the localization of two true-minimum conformers, *s-cis* and *s-trans*, and one transition

Table 2. ⁷⁷ Se ⁻¹ H spin-spin coupling constants of selenophene calculated at different levels of theory ^a											
Coupling constant	Method	Basis set	J _{DSO}	$J_{\rm PSO}$	J_{SD}	$J_{\rm FC}$	J	Exp. ^b			
² J(Se,H-2)	SOPPA	cc-pVDZ	-0.21	-4.32	-0.12	48.63	43.98	47.6			
		cc-pVTZ	-0.21	-4.56	-0.14	60.18	55.27				
		aug-cc-pVTZ	-0.21	-4.59	-0.14	58.11	53.17				
		aug-cc-pVTZ-J	-0.21	-4.83	-0.01	51.45	46.40				
		cc-pVDZ-su2	-0.21	-4.85	-0.19	51.04	45.79				
		cc-pVTZ-su2	-0.21	-4.65	-0.18	51.15	46.11				
	SOPPA(CCSD)	cc-pVDZ	-0.21	-4.19	-0.11	47.26	42.75				
		cc-pVTZ	-0.21	-4.50	-0.13	58.00	53.16				
		aug-cc-pVTZ	-0.21	-4.55	-0.13	56.03	51.14				
		aug-cc-pVTZ-J	-0.21	-4.81	0.00	49.60	44.58				
		cc-pVDZ-su2	-0.20	-4.72	-0.17	49.37	44.28				
		cc-pVTZ-su2	-0.21	-4.60	-0.17	49.28	44.30				
	DFT-B3LYP	cc-pVDZ	-0.21	-5.11	-0.19	57.21	51.70				
		cc-pVTZ	-0.21	-5.60	-0.22	71.83	65.80				
		aug-cc-pVTZ	-0.21	-5.64	-0.22	68.19	62.12				
		aug-cc-pVTZ-J	-0.21	-5.93	-0.07	58.62	52.41				
		cc-pVDZ-su2	-0.21	-5.65	-0.24	58.68	52.58				
		cc-pVTZ-su2	-0.21	-5.69	-0.24	58.63	52.49				
³ J(Se,H-3)	SOPPA	cc-pVDZ	-0.35	0.14	0.31	15.59	15.69	9.4			
		cc-pVTZ	-0.35	-0.10	0.35	17.00	16.90				
		aug-cc-pVTZ	-0.35	-0.08	0.35	13.70	13.62				
		aug-cc-pVTZ-J	-0.35	0.08	0.12	9.97	9.82				
		cc-pVDZ-su2	-0.35	-0.04	0.30	9.33	9.24				
		cc-pVTZ-su2	-0.35	-0.10	0.34	9.82	9.71				
	SOPPA(CCSD)	cc-pVDZ	-0.35	0.13	0.30	15.16	15.24				
		cc-pVTZ	-0.35	-0.12	0.34	16.18	16.05				
		aug-cc-pVTZ	-0.35	-0.09	0.34	13.01	12.91				
		aug-cc-pVTZ-J	-0.35	0.07	0.11	9.40	9.23				
		cc-pVDZ-su2	-0.35	-0.05	0.29	9.05	8.94				
		cc-pVTZ-su2	-0.35	-0.11	0.33	9.34	9.21				
	DFT-B3LYP	cc-pVDZ	-0.35	0.06	0.41	12.97	13.09				
		cc-pVTZ	-0.35	-0.24	0.44	14.92	14.77				
		aug-cc-pVTZ	-0.35	-0.20	0.44	11.66	11.55				
		aug-cc-pVTZ-J	-0.35	-0.05	0.23	7.74	7.75				
		cc-pVDZ-su2	-0.35	-0.15	0.39	7.69	7.58				
		cc-pVTZ-su2	-0.35	-0.24	0.43	7.87	7.71				
^a All couplings and cou	pling contributions in	Hz.									

^b Measured in CDCl₃, this work.

state, TS, for all compounds of this series. All localized conformers and transition states of **4–7** optimized at the MP2/6-311G** level subject to solvent effect (CDCl₃) within the PCM model are shown in Fig. 1. The harmonic frequency analysis revealed no imaginary frequencies for the former (conformers) and showed only one imaginary frequency for each of the latter (transition states).

It is noteworthy that both conformers in the series of **4–7** are ideally planar, providing no out-of-plane deviations while all transition states are almost ideally orthogonal. Compounds **4**, **5** and **7** adopt predominant *s-cis* conformation, in line with early experimental findings by Simonnin *et al.*^[37] for 2-formylselenophene (**4**), while 2-carboxyselenophene (**6**) exists in an almost equimolar mixture of both conformers, *s-cis* and *s-trans*. Interestingly, (2-selenophenyl)aldoxime (**7**) has an unusual aldoximes *Z* configuration derived here from the experimental value of ¹*J*(C,H) = 175.0 Hz (calculated values for Z and E isomers

are 177.1 and 169.5 Hz respectively) and confirmed by MP2/6-311G^{**} calculations demonstrating energetic preference of *Z* isomer of **7** as compared to *E* isomer by 4.4 kJ/mol considered in their predominant conformations. Results of this theoretical energy-based conformational analysis of **4–7** are summarized in Table 5.

It follows from the data presented in Tables 3 and 4 that generally a good agreement is observed between experimental and final calculated ⁷⁷Se⁻¹H spin-spin coupling constants (conformationally averaged for **4–7**) in the whole series of compounds **1–7** for both basis sets, aug-cc-pVTZ-J and cc-pVTZ-su2, demonstrating the adequacy of the level of theory and good quality of both basis set. However, in the future computations of ⁷⁷Se⁻¹H couplings, it should be kept in mind that the latter is much less computationally demanding. Indeed, aug-cc-pVTZ-J contains 83 basis functions for selenium as compared to 59 functions in

Table 3.	⁷⁷ Se- ¹ H spin-spin coupling constants of 2-substituted selenophenes calculated at the SOPPA/aug-cc-pVTZ-J level ^a								
Cmpd.	Coupling constant	Conformer ^b	J _{DSO}	J _{PSO}	$J_{\rm SD}$	$J_{\rm FC}$	J	Calculated ^c	Experiment ^d
1	² <i>J</i> (Se,H-2)	e)	-0.21	-4.83	-0.01	51.45	46.40	46.40	47.6
	³ J(Se,H-3)	e)	-0.35	0.08	0.12	9.97	9.82	9.82	9.4
2	² J(Se,H-5)	e)	-0.18	-4.62	-0.17	50.51	45.54	45.54	46.9
	³ <i>J</i> (Se,H-3)	e)	-0.33	0.09	0.23	5.17	5.16	5.16	4.5
	³ J(Se,H-4)	e)	-0.33	0.12	0.38	8.00	8.17	8.17	7.0
3	² J(Se,H-5)	e)	-0.20	-5.49	-0.28	50.79	44.82	44.82	48.3
	³ <i>J</i> (Se,H-3)	e)	-0.34	0.08	0.41	4.72	4.87	4.87	3.9
	³ J(Se,H-4)	e)	-0.34	0.21	0.37	8.05	8.29	8.29	7.8
4	² J(Se,H-5)	s-cis	-0.18	-5.63	-0.13	47.93	41.99	42.06	45.6
		s-trans	-0.19	-5.58	-0.10	49.72	43.85		
	³ <i>J</i> (Se,H-3)	s-cis	-0.33	-0.16	0.04	5.54	5.09	5.14	4.9
		s-trans	-0.33	-0.06	0.10	6.43	6.14		
	³ <i>J</i> (Se,H-4)	s-cis	-0.33	-0.04	0.11	7.07	6.81	6.91	6.9
		s-trans	-0.34	-0.04	0.28	9.34	9.24		
	³ J(Se,H _{CO})	s-cis	-0.27	0.08	0.08	9.51	9.40	9.11	8.4
		s-trans	0.08	-0.02	-0.16	-2.25	-2.35		
5	² <i>J</i> (Se,H-5)	s-cis	-0.18	-5.64	-0.25	47.06	40.99	41.22	44.8
		s-trans	-0.18	-5.39	-0.23	50.13	44.33		
	³ <i>J</i> (Se,H-3)	s-cis	-0.32	-0.09	0.35	6.10	6.04	6.06	5.5
	_	s-trans	-0.32	-0.02	0.32	6.36	6.34		
	³ J(Se,H-4)	s-cis	-0.33	-0.04	0.34	6.46	6.43	6.65	6.7
		s-trans	-0.33	-0.01	0.33	9.55	9.54		
6	² J(Se,H-5)	s-cis	-0.19	-5.70	-0.27	48.12	41.96	42.19	45.3
		s-trans	-0.19	-5.65	-0.28	48.55	42.43		
	³ <i>J</i> (Se,H-3)	s-cis	-0.32	0.03	0.41	5.41	5.53	5.42	5.5
	2	s-trans	-0.32	0.01	0.37	5.25	5.31		
	³ J(Se,H-4)	s-cis	-0.33	0.00	0.34	7.05	7.06	7.50	7.6
		s-trans	-0.33	-0.01	0.34	7.96	7.96		
7	² J(Se,H-5)	s-cis	-0.18	-5.71	-0.36	46.07	39.82	39.91	42.4
	2	s-trans	-0.19	-5.20	-0.21	54.41	48.81		
	³ J(Se,H-3)	s-cis	-0.32	-0.10	0.23	5.58	5.39	5.43	5.1
	2	s-trans	-0.31	0.25	0.43	8.60	8.97		
	³ J(Se,H-4)	s-cis	-0.33	-0.05	0.33	6.27	6.22	6.25	6.0
	3//(-11)	s-trans	-0.33	0.13	0.35	9.08	9.23	10.00	177
	J(Se,H _{CN})	s-CIS	-0.27	-0.16	0.14	19.29	19.0 5.12	18.80	17.7
		s-trans	0.10	-0.07	-0.12	5.22	5.13		

^a All couplings and coupling contributions in Hz.

^b Optimized structures are shown in Fig. 1.

^c Total calculated couplings, conformationally averaged for **4–7** subject to conformers populations, see Table 5.

 $^{\rm d}$ Measured in CDCl₃, this work.

^e Stationary true-minimum equilibrium geometries.

cc-pVTZ-su2. Furthemore, double-zeta analog of the latter, ccpVDZ-su2, also showing good results for selenophene (Table 2), uses only 38 basis functions, and this may be of crucial importance in the calculations of larger organoselenium species. As observed, it is typical that the Fermi-contact term is by far dominant for both types of ⁷⁷Se-¹H couplings, geminal and vicinal, while the noncontact contributions are next to negligible except for the relatively large and negative paramagnetic spin-orbital term of -(5-6) Hz in the case of all geminal couplings ²J(Se,H-5) in the series of **1–7**.

It is noteworthy that in the conformationally labile selenophenes **4–7**, all vicinal couplings, ³*J*(Se,H-3), ³*J*(Se,H-4) and ³*J*(Se,H_X), differ noticeably in the *s-cis* and *s-trans* conformers, and this difference

is mostly pronounced for the latter, ³*J*(Se,H_X), amounting to *ca* 12 Hz in **4** and to *ca* 14 Hz in **7**. Apparently, the reason of this striking difference originates in the orientation of the substituent bearing the C = X (X = O, N) bond. Similar strong conformation dependences of spin-spin couplings of other types on internal rotation in the vicinity of carboxyl group were reported earlier for carbohydrates and other organic systems.^[38]

To examine this orientational effect, we have calculated the dihedral angle dependences of the title couplings with respect to the internal rotation of the substituent at the C-2 position of the selenophene ring (Figs 2–4). As follows from these data, indeed, all vicinal 77 Se $^{-1}$ H couplings demonstrate a remarkable stereochemical behavior and thus provide an obvious versatile

Table 4.	ible 4. ⁷⁷ Se ⁻¹ H spin-spin coupling constants of 2-substituted selenophenes calculated at the SOPPA/cc-pVTZ-su2 level ^a									
Cmpd.	Coupling constant	Conformer ^b	J _{DSO}	J _{PSO}	J_{SD}	$J_{\rm FC}$	J	Calculated ^c	Experiment ^d	
1	² J(Se,H-2)	e	-0.21	-4.65	-0.18	51.15	46.11	46.11	47.6	
	³ J(Se,H-3)	e	-0.35	-0.10	0.34	9.82	9.71	9.71	9.4	
2	² <i>J</i> (Se,H-5)	e	-0.19	-4.51	-0.18	50.24	45.36	45.36	46.9	
	³ <i>J</i> (Se,H-3)	e	-0.33	-0.12	0.22	5.05	4.82	4.82	4.5	
	³ J(Se,H-4)	e	-0.33	-0.08	0.36	7.91	7.86	7.86	7.0	
3	² J(Se,H-5)	e	-0.19	-5.36	-0.28	50.45	44.62	44.62	48.3	
	³ <i>J</i> (Se,H-3)	e	-0.33	-0.09	0.39	4.55	4.52	4.52	3.9	
	³ J(Se,H-4)	e	-0.34	-0.01	0.34	7.98	7.97	7.97	7.8	
4	² <i>J</i> (Se,H-5)	s-cis	-0.18	-5.51	-0.28	47.58	41.61	41.71	45.6	
		s-trans	-0.19	-5.41	-0.23	49.74	43.91			
	³ <i>J</i> (Se,H-3)	s-cis	-0.33	-0.33	0.27	5.44	5.05	5.09	4.9	
		s-trans	-0.33	-0.23	0.34	6.22	6.00			
	³ <i>J</i> (Se,H-4)	s-cis	-0.33	-0.25	0.30	7.09	6.81	6.90	6.9	
		s-trans	-0.33	-0.22	0.28	9.23	8.96			
	³ J(Se,H _{CO})	s-cis	-0.27	0.06	0.08	9.75	9.62	9.33	8.4	
		s-trans	0.08	-0.05	-0.13	-2.24	-2.34			
5	² J(Se,H-5)	s-cis	-0.19	-5.53	-0.24	46.71	40.75	40.98	44.8	
		s-trans	-0.19	-5.26	-0.22	49.62	43.95			
	³ <i>J</i> (Se,H-3)	s-cis	-0.32	-0.26	0.34	6.01	5.77	5.79	5.5	
	2	s-trans	-0.32	-0.19	0.31	6.14	5.94			
	³ J(Se,H-4)	s-cis	-0.33	-0.25	0.32	6.48	6.22	6.43	6.7	
		s-trans	-0.33	-0.20	0.30	9.45	9.22			
6	² <i>J</i> (Se,H-5)	s-cis	-0.18	-5.57	-0.26	47.76	41.75	41.95	45.3	
	2	s-trans	-0.18	-5.52	-0.26	48.13	42.17			
	³ <i>J</i> (Se,H-3)	s-cis	-0.32	-0.13	0.40	5.29	5.24	5.10	5.5	
	2.000 00 00	s-trans	-0.32	-0.16	0.35	5.08	4.95			
	³ J(Se,H-4)	s-cis	-0.33	-0.20	0.31	7.05	6.83	7.25	7.6	
	2	s-trans	-0.33	-0.20	0.31	7.91	7.69			
7	² J(Se,H-5)	s-cis	-0.18	-5.58	-0.34	45.70	39.60	39.66	42.4	
	2	s-trans	-0.19	-5.02	-0.16	51.58	46.21			
	³ J(Se,H-3)	s-cis	-0.32	-0.26	0.22	5.46	5.10	5.14	5.1	
	3.45 11 1)	s-trans	-0.31	0.06	0.41	8.36	8.52	6.40	6.0	
	³ J(Se,H-4)	S-CIS	-0.32	-0.24	0.31	6.34	6.09	6.12	6.0	
	3/(50 H)	s-trans	-0.33	-0.07	0.33	8.96 10.02	8.89	10 57	177	
	-J(Se,H _{CN})	s-CIS	-0.27	-0.17	0.13	19.0Z	10./1	10.57	17.7	
		s-trans	0.10	-0.10	-0.11	5.10	4.99			

^a All couplings and coupling contributions in Hz.

^b Optimized structures are shown in Fig. 1.

^c Total calculated couplings, conformationally averaged for **4–7** subject to conformers populations, see Table 5.

^d Measured in CDCl₃, this work.

^e Stationary true-minimum equilibrium geometries.

tool for the stereochemical analysis of the organoselenium compounds. However, the most encouraging finding is a striking dihedral angle dependence of ${}^{3}J(Se,H_X)$, which is due to their Karplus-type behavior, as is well known for many types of spin–spin coupling constants. Here, we do not discuss this aspect in detail, and address the reader to the key reviews.^[39]

Concluding Remarks

A very good performance of the high-level *ab initio* method, SOPPA, in combination with Sauer's basis set, aug-cc-pVTZ-J, extended in this paper for the selenium atom has been demonstrated in the calculations of 77 Se $^{-1}$ H spin-spin coupling constants in the series

of 2-substituted selenophenes. This is especially encouraging with respect to the marked stereochemical behavior of 77 Se $^{-1}$ H couplings, providing a versatile tool for the conformational analysis of the related organoselenium compounds.

Experimental

NMR measurements

 77 Se NMR spectra were recorded on a Bruker AVANCE 400 MHz spectrometer (77 Se, 76.34 MHz) in a 5-mm broadband probe at 25 °C in CDCl₃. Experimental measurements of 77 Se $^{-1}$ H spin $^{-}$ spin coupling constants were carried out from the proton-coupled



Figure 1. Equilibrium structures of the localized true-minimum conformers and transition states of the conformationally labile 2-substituted selenophenes 4-7 in CDCl₃ optimized at the MP2/6-311G^{**} level subject to solvent effect within the PCM model. Relative energies are given in parentheses (kJ/mol) and dihedral angles are shown with arrows. Element colors: selenium – brown; oxygen – red, nitrogen – blue; carbon – yellow; hydrogen – gray.

Table 5. Conformations of 2-substituted selenophenes 4–7 localized at the MP2/6-311G** level										
Compound	Confor-mation ^a	Туре	Relative energy (kJ/mol)	Population (%)	Dihedral angle (degree)	Imaginary frequency (cm^{-1})				
4	s-cis	Conformer	0.0	95	0	-				
	s-trans	Conformer	7.4	5	180	-				
	TS	Transition state	46.1	-	90	154.2				
5	s-cis	Conformer	0.0	93	0	-				
	s-trans	Conformer	6.5	7	180	-				
	TS	Transition state	38.6	-	91	77.2				
6	s-cis	Conformer	0.0	51	0	-				
	s-trans	Conformer	0.1	49	180	-				
	TS	Transition state	36.4	-	89	86.0				
7	s-cis	Conformer	0.0	99	0	-				
	s-trans	Conformer	11.9	1	180	-				
	TS	Transition state	33.0	-	93	52.3				
^a Shown in Fig. 1.										

 77 Se NMR spectra (either 1D or 2D) using the spectral settings as follows: 90° pulse length, 13 μ s; spectral width, 8 kHz; acquisition time, 8.5 s; relaxation delay, 3 s; digital resolution 0.06 Hz/pt; accumulation time, 1 h.

Computational details

All geometry optimizations were performed with the GAMESS code^[40] at the MP2/6-311G^{**} level, taking into account solvent effect of CDCl₃ within the PCM model. Calculations of spin-spin coupling constants were carried out at the DFT-B3LYP, SOPPA and SOPPA(CCSD) levels of theory taking into account all four nonrelativistic coupling contributions with the DALTON package.^[41]

Synthesis

Selenophene (1) was obtained by the thermolysis of diethyl selenide and acetylene in the presence of methanol.^[42] 2-Chloroselenophene (2), 2-cyanoselenophene (3) and 2-formylselenophene (4) were synthesized from selenophene, as described in Refs.,^[43-45] while 2-carboxyselenophene (6) and (2-selenophenyl)aldoxime (7) were synthesized from the parent 2-formylselenophene (4), as described in Refs. [44,45]

2-Acetylselenophene (5) was prepared by the improved procedure.^[46] To a stirred mixture of anhydrous AlCl₃ (6.17 g, 46 mmol) in dichloromethane (100 ml) under argon at -15 °C, an acetyl chloride (46 mmol) was added portion-wise for 0.5 h. The reaction mixture was stirred for 0.5 h, then selenophene (6.07 g,



Figure 2. Dihedral angle dependences of ³*J*(Se,H-3) of 2-substituted selenophenes **4–7** calculated at the SOPPA/aug-cc-pVTZ-J level. The value of $\varphi = 0^{\circ}$ is assigned to the *cisoid* orientation of Se–C² and C=O (C=N) bonds.



Figure 3. Dihedral angle dependences of ³*J*(Se,H-4) of 2-substituted selenophenes **4–7** calculated at the SOPPA/aug-cc-pVTZ-J level. The value of $\varphi = 0^{\circ}$ is assigned to the *cisoid* orientation of Se–C² and C=O (C=N) bonds.

46 mmol) was introduced dropwise for 2.5 h. The reaction mixture was allowed to reach ambient temperature and then was stirred for another 1 h. The reaction mixture was poured on crushed ice and the residue in the flask was treated with water and CH₂Cl₂ until complete dissolution. The liquids were combined and the organic layer was separated and the aqueous layer was extracted with CH₂Cl₂. The extract was washed with water and dried over MqSO₄. After evaporation of the extractant and vacuum distillation of the residue, ketone 5 was obtained. Light-yellow liquid (48%); bp 84–89 (5 mm Hg); ¹H NMR (400.13 MHz, CDCl₃): $\delta = 8.34$ (dd, ${}^{3}J_{4-5} = 5.5$ Hz, ${}^{4}J_{3-5} = 1.0$ Hz, 1 H, H-5), 7.87 (dd, ${}^{3}J_{4-3} = 3.9$ Hz, ${}^{4}J_{3-5} = 1.0$ Hz, 1 H, I-3), 7.36 (dd, ${}^{3}J_{4-5} = 5.5$ Hz, ${}^{3}J_{4-3} = 3.9$ Hz, 1 H, I-4), 2.53 ppm (s, 3 H, Me); ¹³C NMR (100.62 MHz, CDCl₃): $\delta = 191.61 \text{ (C=O)}, 151.27 \text{ (C-2)}, 139.90 \text{ (C-5)}, 134.87 \text{ (C-3)}, 130.61$ (C-4), 25.94 ppm (Me); IR (film): $\nu = 3096$, 3000, 2922, 2360, 2342, 1654, 1529, 1358, 1311, 1269, 1086, 1046, 1021, 919, 849, 801, 710, 633, 601, 557 cm⁻¹; (FAB–MS) (HRMS) MS: *m/z*: (for ⁸⁰Se, *I*, %): 174 (27.7) [M]^{+,}, 159 (32.7) [M-CH₃]⁺, 131 (11.1) [C₄H₃Se]⁺, 105 (6.5) [C₂HSe]⁺, 93 (2.6) [CHSe]⁺, 80 (2.9) [Se]⁺, 65 (2.8) [C₅H₅]⁺, 50 $(13.8) [C_4H_2]^+$; elemental analysis: calcd. (%) for C₆H₆OSe (173.07): C 41.63, H 3.47, Se 45.65; found: C 41.52, H 3.49, Se 46.0.

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Figure 4. Dihedral angle dependences of ³*J*(Se,H_X) of 2formylselenophene (**4**) and (2-selenophenyl)aldoxime (**7**) calculated at the SOPPA/aug-cc-pVTZ-J level. The value of $\varphi = 0^{\circ}$ is assigned to the *cisoid* orientation of Se-C² and C=O (C=N) bonds.

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