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^{77}Se NMR. Observation of $^3J_{\mathrm{Se-Se}}$ Couplings Allowing Cis/Trans Isomer Assignments in Substituted Tetraselenafulvalenes†

Ib Johannsen* and Hanne Eggert*

Contribution from the Physics Laboratory III, Technical University of Denmark, DK-2800 Lyngby, Denmark, and Department of General and Organic Chemistry, University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen Ø, Denmark.

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Abstract: ^{77}Se chemical shifts and ^{1}H–^{77}Se and ^{77}Se–^{77}Se coupling constants Denmark,DK-2800 for a series of substituted tetraselenafulvalenes (TSFs). For mixtures of cis and trans isomers resolved signals for each isomer were observed at 21 kG. The cis/trans assignments were obtained by measurement of the homonuclear ^3J selenium-77 coupling constant. This coupling constant is related to dihedral bond angles; large coupling constants (80–100 Hz) are observed for cis orientation of the atoms, while trans arrangement gives rise to numerically much smaller values (10–25 Hz). A ^5J hydrogen–selenium-77 coupling constant of ~5 Hz was measured. This is shown to be connected to an all-trans arrangement of the atoms in the coupling path and can also provide cis/trans isomer assignments in TSFs.

Introduction

Interest in tetraselenafulvalenes (TSF) (see Figure 1) derives primarily from their use as constituents in organic metals. Since the discovery of the first metallic organic charge-transfer complex,[1,2] a tetrathiafulvalene complex, there has been a continuous interest in the design and synthesis of new organic metals.[3,4] With the recent discovery of superconductivity in salts of tetramethyl-TSF,[5] the investigation of donors derived from TSF has been given increased attention.[6]

Because of the high symmetry in fulvalene donors, usual spectroscopic methods (IR, UV, MS, ^{1}H and ^{13}C NMR) provide little information on the structure and isomeric purity of these systems. For substituted TSFs where cis/trans isomerism is possible, this creates a difficult problem. The cis and trans isomers (see Figure 1) are both formed in the synthesis, and so far it has been practically impossible to determine the ratio of isomers present in a given mixture. This has hampered a possible separation of the isomers, and only mixtures of isomers with variable and unknown isomeric ratios have been investigated as donors in organic metals.[7,8] Because the physical properties of the resulting organic metals are very sensitive to impurities and disorder in the crystal lattice, it is of major importance to be able to monitor isomer ratios and identify individual isomers.

^{77}Se NMR appears to be the method of choice. The ^{77}Se nuclei have a spin of 1/2 and a relatively high natural abundance (7.6%). The receptivity is a factor of 3 better than that of ^{13}C,[9] a great advantage when studying some of the very sparingly soluble TSF derivatives. The large spread in shielding of ^{77}Se, ~2500 ppm compared with ~250 ppm for ^{13}C, combined with narrow lines ($\Delta_{\nu 1/2}$ are normally <1 Hz) results in an extraordinary high spectral resolution in ^{77}Se NMR.

We have undertaken a ^{77}Se NMR study of TSFs in order to provide background data for analytical applications and to obtain parameters that can be related to structure and stereochemistry of substituted TSFs. Our study includes measurements of ^{77}Se–^{77}Se coupling constants, a versatile but, until now, unexplored tool in structure determination of organic selenium compounds. It is shown that ^{77}Se NMR can solve not only the problem of isomer ratio determination, but it also allows the cis/trans isomer assignment.

Experimental Section

TSF and dibenzo-TSF were prepared according to procedures given in literature.[10,11] Dimethyl-, diphenyl-, tetramethyl-, diethyldimethyl-, and dicarboxyethyl-TSF were prepared by $(CH_3O)_3P$ coupling of the corresponding 1,3-diselenole-2-selones, which were synthesized using the "carbamate" route.[12-14] *trans-* and *cis*-1,2-bis(methylseleno)-1-phenylethylene were prepared by refluxing (2 h) phenylacetylene and dimethyldiselenide in tetrahydrofuran solution using sodium ethanolate (1 equiv) as catalyst. The products were isolated by column chromatography (silica, toluene) followed by preparative TLC (silica, hexane). Previously, this reaction has been reported to result only in the trans isomer.[15]

The ^{77}Se NMR spectra were recorded at 17.04 MHz using a JEOL FX 90Q NMR instrument equipped with a broad-band probe. Chemical shifts and ^{77}Se–^{77}Se coupling constants were measured with complete proton decoupling. Chemical shifts and coupling constants were determined with a maximum of 0.49 Hz per data point. Chemial shifts are referenced to external dimethylselenide in C_6D_6 (1 M) (reference frequency 48767.8 Hz) by frequency difference calculations. The probe temperature was held between 29 and 30 °C for all measurements. The spectra were obtained from 0.02–0.1 M solutions (depending on solubility) in CS_2 with ~20% C_6D_6 added as a lock substance.

The nuclear Overhauser enhancement experiments were performed at 270 MHz on a Bruker Hx 270 FT instrument on $CDCl_3$ solutions at 30 °C. The enhancements were obtained from ^{1}H-{^{1}H} NOE difference spectra; eight scans with irradiation on and eight scans with irradiation removed from resonance were accumulated alternately and stored separately. The irradiation was gated on during a waiting time of at least 15 s prior to each scan. Two ^{1}H-{^{1}H} NOE difference spectra were obtained for each isomer of 1,2-bis(methylseleno)-1-phenylethylene, in all cases irradiating the protons of a selenomethyl group and observing the signal of the vinylic hydrogen atom. The enhancements are 6 and 3% for one isomer, and 10 and <0.5% for the other isomer, when irra-

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† Systematic name: $\Delta^{2,2'}$-bis(1,3-diselenolylidene).

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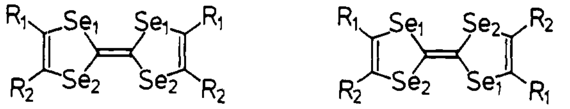
Table I. ^{77}Se Chemical Shifts (ppm) and ^{77}Se–^{1}H Coupling Constants (Hz) of Tetraselenafulvalenes[a]

						$^{3}J_{Se-H}$		
	R_1	R_2	$\delta(^{77}$Se-1)	$\delta(^{77}$Se-2)	$^{2}J_{Se-H}$	vinylic H	alkyl H	$^{5}J_{Se-H}$
	H	H	618.9	618.9	55.7	9.7		5.4
	CH_3	CH_3	673.1	673.1			13.2	
	-CH=CHCH=CH-		610.2	610.2		*b*		
cis	CH_3	H	642.6			7.8	11.7	4.9
				626.4	56.2			
trans	CH_3	H	636.4			7.8	11.7	
				632.6	56.2			4.9
cis	Ph	H	625.3			6.8		4.9
				647.9	55.2			
trans	Ph	H	619.9			6.6		
				653.3	55.0			4.4
cis	COOEt	H	625.6			4.4		4.4
				656.7	53.2			
trans	COOEt	H	618.8			4.4		
				664.6	53.2			4.9
cis	CH_3	CH_2CH_3	672.7				13.2	
				651.3			15.9	
trans	CH_3	CH_2CH_3	672.8				13.2	
				651.4			15.9	

[a] The chemical shifts are in parts per million relative to $(CH_3)_2Se$ (see Experimental Section). [b] Because of coupling of ^{77}Se with the four benzenoid protons, $^{3}J_{Se-H}$ cannot be directly measured.



cis trans

Figure 1. General structures of the tetraselenafulvalenes.

diating low- and high-field methyl groups, respectively. Thus, the isomer showing sizable NOE at both methyl groups is assigned the trans isomer, and the isomer with significant NOE at only one methyl group is the cis isomer.

Results and Discussion

Chemical Shifts. The ^{77}Se chemical shifts of the compounds examined are given in Table I. For the disubstituted TSFs, the assignment of peaks to the nonequivalent selenium atoms, Se-1 and Se-2, was based on the expected (see below) large difference between the size of two and three bond coupling constants of selenium to vinylic hydrogen atoms ($^{2}J_{Se-H}$ = 53–56 Hz and $^{3}J_{Se-H}$ = 4–10 Hz). In the tetrasubstituted dimethyl-diethyl-TSFs, the assignments to Se-1 and Se-2 followed from the different multiplicities (quartets and triplets) of the three bond couplings, $^{3}J_{Se-H}$.

Spectra of cis/trans isomeric compounds were determined as mixtures of both. The proton noise-decoupled ^{77}Se NMR spectra of these mixtures all display four well-resolved lines corresponding to separate signals for cis and trans isomeric compounds. Thus, determination of isomer ratio for a cis/trans mixture is straightforward using ^{77}Se NMR spectra. Most impressive is this finding for the cis and trans isomers of dimethyl-diethyl-TSF, the spectrum of which is shown in Figure 2. In this case a minor change in structure six bonds away from a selenium nucleus results in a resolved difference in chemical shifts of 0.1 ppm.

As seen from the spectrum in Figure 2, the present sample dimethyl-diethyl-TSF contained unequal amounts of the two isomers. Distinguishing between pairs of signals from the two isomers could be done on the basis of the intensities alone. In general, however, the samples of disubstituted TSFs studied appeared as mixture of equal amounts cis and trans isomers. For these compounds cis/trans signal connections are determined on the basis of $^{5}J_{Se-H}$ or $^{3}J_{Se-Se}$ coupling constants as described below.

The ^{77}Se chemical shifts for the present series of closely similar compounds cover more than 60 ppm with dibenzo-TSF found at highest and tetramethyl-TSF at lowest field. With electron-attracting substituents (Ph and COOEt) in sym-disubstituted TSFs, the vicinally placed Se atoms, Se-2, are found downfield 25–40 ppm relative to the parent molecule, TSF. The chemical shift of the geminally placed Se-1 nuclei is only slightly affected. Substituting the parent molecule with weakly donating groups, as in dimethyl-TSF, the difference in chemical shifts of Se-1 and Se-2 gets much smaller and Se-1 is in this case shifted downfield relative to Se-2.

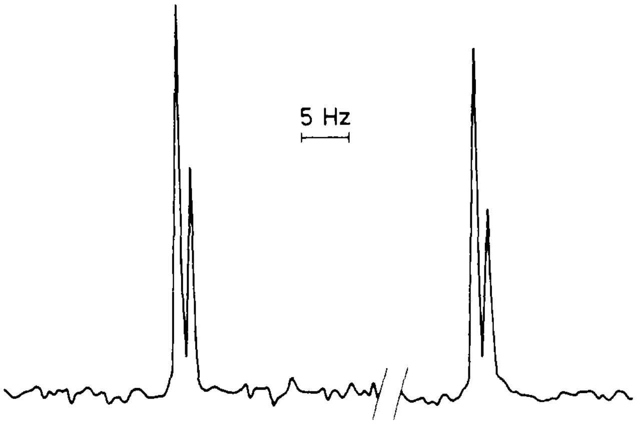


Figure 2. The complete proton-decoupled ^{77}Se NMR spectrum of the cis and trans dimethyl-diethyl-TSF mixture.

The ^{77}Se chemical shifts of the TSFs are found to be quite sensitive to changes in solvent and concentration. In the *sym*-disubstituted TSFs this dependence is even more pronounced for Se-2 than Se-1. Differences between chemical shifts of $CDCl_3$ and CS_2/C_6D_6 solutions of dimethyl-TSF are 10 and 6 ppm for Se-2 and Se-1 nuclei, respectively, thus demonstrating a strong and specific solvent–dimethyl-TSF interaction. In addition, chemical shifts of the TSFs display a temperature dependence of ~0.1 ppm/deg (low-field shifts with increasing temperature). As with the solvent dependence, the change in temperature has different effects on Se-1 and Se-2. The Se nuclei with the larger solvent dependence also show the larger temperature dependence. In selenium-containing transition metal complexes similar dependences of ^{77}Se chemical shifts upon solvent and temperature have been observed by Pan and Fackler.[16] They suggested that thermal motion involving solvent–solute interactions may be sufficiently temperature sensitive to produce the observed temerature dependence. The results for the TSFs appear to support this hypothesis. Further work is in progress on solvent and temperature effects on different selenium compounds including diselenides. The ^{77}Se chemical shifts of diselenides are reported[17] to show a strong temperature dependence.

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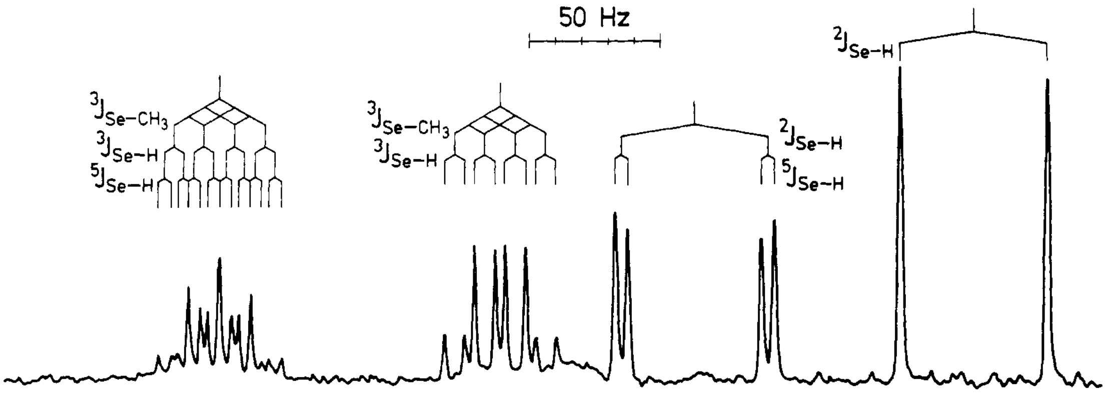

Figure 3. The proton-coupled ^{77}Se NMR spectrum of the cis and trans dimethyl-TSF mixture.

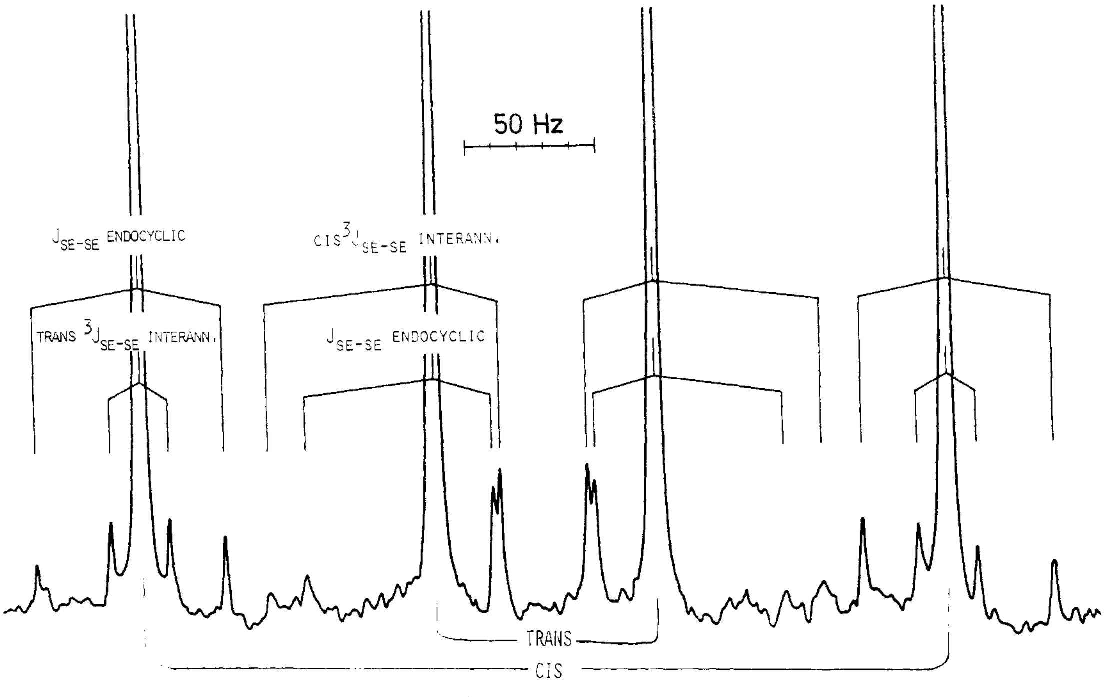

Figure 4. The selenium satellites of the proton noise-decoupled ^{77}Se NMR spectrum of the cis and trans dimethyl-TSF mixture.

^{77}Se–^{1}H Coupling Constants. The proton-coupled spectra of all substituted TSFs are all amenable to first-order analysis. Table I gives the absolute values of the ^{77}Se–^{1}H coupling constants found. In the spectra of sym-disubstituted TSFs the ^2J and ^3J selenium coupling to vinylic hydrogen atoms are assigned in accordance with results on other selenium compounds[18] containing analogous structural features (e.g., selenophene[19] $^2J_{Se-H}$ = 47.3 Hz and $^3J_{Se-H}$ = 9.3 Hz). In Figure 3, showing the proton-coupled spectrum of a cis/trans dimethyl-TSF mixture, two additional types of couplings are observed. A quartet splitting of the two Se-1 signals, due to coupling with the methyl protons ($^3J_{Se-CH_3}$), and a doublet splitting of 4.9 Hz of two selenium signals, one Se-1 and one Se-2 signal. This last type of splitting is seen generally in sym-disubstituted TSFs and is assigned to an interannular coupling of selenium to the vinylic hydrogen atom, $^5J_{Se-H}$. This makes it possible to divide the four signals in the spectra of the disubstituted TSFs into two pairs, each arising from one isomer. Thus, the two signals showing long-range coupling can either be assigned to Se-1 in a cis and Se-2 in a trans isomer or vice versa. However, final cis/trans isomer assignment is not possible from these data alone.

The proton-coupled spectrum of TSF exhibits a second-order pattern. It consists of five triplets symmetrically arranged about the chemical shift. The inner and outer pairs of triplets are separated by 47.8 and 65.4 Hz, respectively. The fifth triplet at the center is of very low intensity. Assuming absence of interannular ^{1}H–^{1}H coupling in TSF, the observed triplet splittings, all of 2.7 Hz, are the average of the two interannular $^5J_{Se-H}$ coupling constants. In the sym-disubstituted TSFs interannular coupling between selenium and hydrogen is observed only for an all-trans arrangement of the nuclei in the coupling path (see below). Application of this relation in the analysis of the TSF spectrum results in a value of 5.4 Hz for the all-trans $^5J_{Se-H}$ interannular coupling constant. In the sym-disubstituted TSFs this coupling constant has a value of 4–5 Hz.

The two- and three-bond selenium–hydrogen coupling patterns have been analyzed as A A′X systems (X = Se).[20] The ^{77}Se satellites in the ^{1}H NMR spectrum of TSF give a value of 7.0 Hz for $J_{AA'}$. The values of selenium–hydrogen coupling constants obtained are given in Table I.

^{77}Se–^{77}Se Coupling Constants. The cis/trans assignment was obtained by means of the observation of selenium satellites in the ^{1}H noise-decoupled ^{77}Se NMR spectra. The $^3J_{Se-Se}$ coupling through the central double bond is the only spectral parameter of the isomers which can be expected to show a difference sufficiently large to allow an isomer assignment. The cis isomer has a trans $^3J_{Se-Se}$ interannular coupling, while the trans isomer correspondingly has a cis coupling. In Figure 4 the satellite

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Table II. ^{77}Se–^{77}Se Coupling Constants (Hz) in Tetraselenafulvalenes

	R_1	R_2	J_{Se-Se} endocyclic	J_{Se-Se} interannular
cis	CH_3	H	72.8	22.7
trans	CH_3	H	73.0	90.7
cis	Ph	H	72.4	21.0
trans	Ph	H	72.4	92.4
cis	COOEt	H	68.8	19.0
trans	COOEt	H	68.8	99.3
cis	CH_3	CH_2CH_3	75.2	22.0
trans	CH_3	CH_2CH_3	75.2	83.7

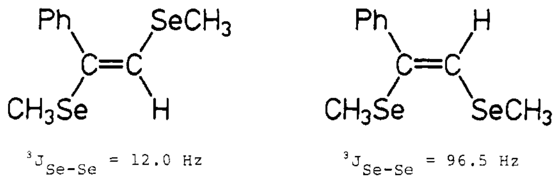

Figure 5. The structure of cis- and trans-1,2-bis(methylseleno)-1-phenylethylene together with the values of the homonuclear selenium coupling constants.

spectrum of the *sym*-dimethyl-TSF is shown and in Table II are given the absolute values of the homonuclear selenium coupling constants of the TSFs. Previously, an attempt has been made to detect $^3J_{Se-Se}$ in a 3-selena-substituted selenophen derivative, but no satellites due to Se–Se couplings were observed; thus, $^3J_{Se-Se}$ is reported to be less than the line width (<2 Hz).[21]

The selenium satellites in the ^{77}Se NMR spectra arise from molecules containing two ^{77}Se isotopes. If the two ^{77}Se nuclei are found on nonequivalent positions, they will couple and result in an AB satellite pattern. The two ^{77}Se nuclei can either be situated in the same ring or be separated with a ^{77}Se nucleus in each ring. Thus, in the proton noise-decoupled spectra of these compounds two satellite patterns appear around each ^{77}Se chemical shift, a $^3J_{Se-Se}$ interannular and a J_{Se-Se} endocyclic. As seen from Table II, one of the coupling constants was within experimental error found to be the same in cis and trans isomeric compounds and therefore assigned to J_{Se-Se} endocyclic. The other coupling constant $^3J_{Se-Se}$ interannular showed large differences between the isomers. The satellite spectra confirm the cis/trans signal connections concluded on the basis of the $^5J_{Se-H}$ coupling constant described above.

In order to relate the observed variation of the interannular $^3J_{Se-Se}$ with specific cis/trans geometry, appropriate model compounds were studied.[22] By the use of ^{1}H-{^{1}H} NOE difference spectroscopy a reliable cis and trans isomer assignment of 1,2-bis(methylseleno)-1-phenylethylene (see Figure 5) was obtained (see Expermental Section for details and NOE values). The homonuclear selenium coupling constants for the cis and trans isomer showed similar large variation with stereochemistry as found for the TSFs. A small transoid coupling constant of 12 Hz was found in the named cis isomer and a much larger cisoid coupling constant of 96 Hz in the named trans isomer. These results gave the final cis/trans assignments given in the tables.

By comparison of the undecoupled spectrum of dimethyl-TSF, Figure 3, with the satellite spectrum of the same sample, Figure 4, it can finally be concluded that the interannular $^5J_{Se-H}$ coupling constant is observed only for selenium nuclei placed all-trans to a vinylic hydrogen atom.

Summary and Conclusion

The results presented in this work show that ^{77}Se chemical shifts in tetraselenafulvalenes are very sensitive to the structural environment of the selenium nucleus. Differences in structure six bonds away lead to resolved ^{77}Se chemical shifts. Thus ^{77}Se NMR is a useful analytical tool in testing purity and isomer ratio, as well as in structure determination of TSFs.

A general relationship between the vicinal couling constant $^3J_{Se-Se}$ in olefins and the stereochemical orientation of the selenium atoms has been established. Large vicinal coupling constants are found for a cis orientation of the atoms while trans arrangement gives rise to numerically much smaller coupling constants.

A large long-range selenium hydrogen coupling constant, $^5J_{Se-H}$ of ~5 Hz, has been observed in the TSFs. This coupling is connected to an all-trans arrangement of the atoms in the coupling path.

Each of the above-mentioned parameters, the $^3J_{Se-Se}$ and $^5J_{Se-H}$ interannular coupling constants, now allows an unambiguous cis/trans isomer assignment for the TSFs.

Registry No. *cis*-TSF (R_1 = CH_3; R_2 = H), 88375-77-3; *trans*-TSF (R_1 = CH_3; R_2 = H), 88375-78-4; *cis*-TSF (R_1 = Ph; R_2 = H), 88326-69-6; *trans*-TSF (R_1 = Ph; R_2 = H), 88326-70-9; *trans*-TSF (R_1 = COOEt; R_2 = H), 88326-71-0; *trans*-TSF (R_1 = COOEt; R_2 = H), 88326-72-1; *cis*-TSF (R_1 = CH_3; R_2 = CH_2CH_3), 88326-73-2; *trans*-TSF (R_1 = CH_3; R_2 = CH_2CH_3), 82357-45-7; TSF (R_1 = R_2 = H), 54489-01-9; TSF (R_1 = R_2 = CH_3), 55259-49-9; TSF (R_1, R_2 = CH=CH—CH=CH), 88326-74-3; ^{77}Se, 14681-72-2.

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[22] Results from a more extensive study of ^{77}Se–^{77}Se coupling constants in relation to molecular structure and stereochemistry will be published soon.