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Intramolecular Nonbonded Interactions Between Divalent Selenium Centers with Donor and Acceptor Substituents

Alberth Lari,[a] Christian Bleiholder,[a,b] Frank Rominger,[a] and Rolf Gleiter*[a]

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To investigate the intramolecular van der Waals interactions between two divalent selenium centers in the solid state and in solution, we have prepared methyl 2-(methylselenyl)benzyl selenide (**1**), ethynyl 2-(methylselenyl)benzyl selenide (**2**), and 2-(methylselenyl)benzyl selenocyanate (**3**). By means of NMR spectroscopic studies we have determined the ^{77}Se NMR chemical shifts of the signals of the Se centers of **1**–**3** and their long-range $^{4}J_{Se,Se}$ coupling constants. These results, and the X-ray structural studies of single crystals of **3** and **11**, a quasi-dimer of **2**, point to an Se···Se van der Waals interaction and short Se···H distances in **1**–**3**. These measurements were supported by quantum chemical calculations on **1**–**3** at the MP2/6-311+g(d)//B98/6-311+g(d) level of theory, which showed a preference for the *endo*$_X$ and *endo*$_H$ conformations of **1**–**3**. This finding was confirmed by calculations of the ^{77}Se NMR chemical shifts of **1**–**3** by GIAO-B98 and GIAO-PBE calculations.

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Introduction

In the solid state and in solution directional forces are essential for building three-dimensional structures with voids, channels, helices, or networks.[1,2] These forces may be covalent or noncovalent. The term "noncovalent" includes a large range of attractive and repulsive forces and includes hydrogen bonds, π–π interactions, and interactions between soft acids and bases. Channel-like structures result mainly from hydrogen bonding. One of the simplest ways to form a channel is by stacking cyclic species on top of each other, interconnected by hydrogen bonds. Cyclic peptides[3,4] or cyclodextrins[5] are only two of the most prominent examples. In addition, tubular species have been prepared through hydrogen bonding between the phenolic OH groups of aromatic rings.[6]

Although close contacts between chalcogen centers in the solid state have been reported in the literature,[7] only two- and three-dimensional networks have been described. However, very recently it has been shown that close contacts between chalcogen centers incorporated into cycles or other rigid structures can lead to tubular structures.[8,9] Our studies on these species[8,9] have revealed that the chalcogen centers of one ring are in close contact with two chalcogen centers of two other rings that are stacked one on top of the other. As a result, a zig-zag arrangement of chalcogen atoms arises. Experiments and calculations have further revealed that chalcogen–chalcogen interactions increase in the order of sulfur, selenium, and tellurium.[10] These results indicate that the interaction can to a first approximation be considered as a p-type lone pair acting as electron donor and a chalcogen–carbon σ* orbital as an electron acceptor.[11] However, recent model calculations have shown that correlation effects have to be considered in order to describe the van der Waals interactions of chalcogen centers properly,[12] in particular when the heavier elements selenium or tellurium are involved.

To find out if such interactions are also present in solution, we have investigated a series of model systems containing two selenium centers in close proximity. We chose selenium compounds, because the ^{77}Se nucleus has a spin of I = 1/2 and, although its natural abundance is only 7.6%, the ^{77}Se NMR chemical shift is very sensitive to the electronic environment of the selenium atom and has a wide range, from –500 to +1110 ppm, in a divalent state with respect to dimethyl selenide.[13] We chose compounds **1**–**3** (Figure 1) as the model systems because the substituents provide, on the one hand, the possibility of a close Se···Se contact and, on the other hand, enough flexibility to choose other conformations. Recent progress in selenium chemistry[14] has facilitated this project.

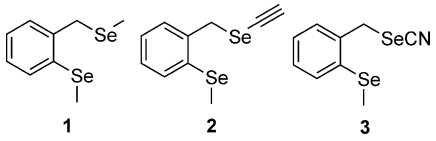

Figure 1. Model systems **1**–**3**.

[a] Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
Fax: +49-6221-544205
E-mail: rolf.gleiter@oci.uni-heidelberg.de
[b] Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106-9510, USA

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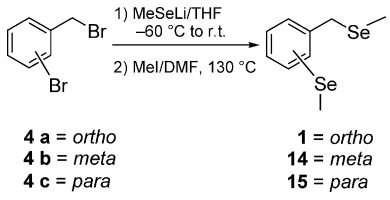
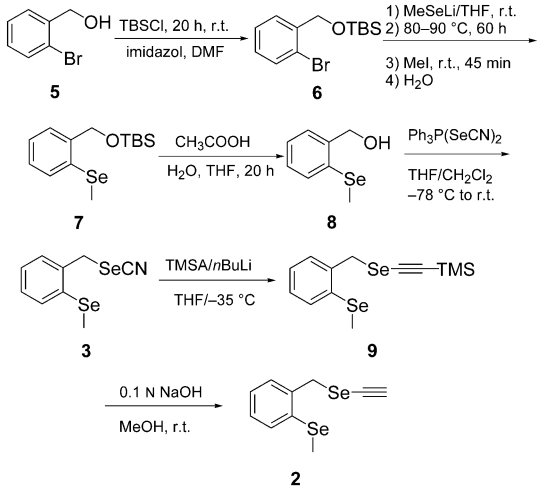
Results and Discussion

Synthesis and Structures of the Model Systems

Compound **1** was prepared in a one-pot reaction by starting with 2-bromobenzyl bromide (**4a**) (Scheme 1). Treatment of **4a** with in situ generated lithium methaneselenolate followed by methylation with methyl iodide[15] yielded **1** as the main product (40%). Compounds **2** and **3** were synthesized commencing with 2-bromobenzyl alcohol (**5**), which, after protection with *tert*-butyldimethylsilyl (TBS) chloride, was treated with lithium methaneselenolate[15] and then methylated to yield **7** (Scheme 2). We used the TBS protecting group, because ethers protected by this substituent have proved to be stable in the presence of *t*BuLi.[16] The TBS group was removed with diluted acetic acid in THF at room temperature to afford the alcohol **8**. The SeCN group was successfully introduced by utilizing $Ph_3P(SeCN)_2$ as the selenocyanation reagent,[17] which was prepared by the addition of an equimolar amount of triphenylphosphane to a freshly prepared solution of selenocyanogen in dichloromethane and THF.[18] By this reaction we obtained **3** in 26% yield. When the selenocyanate **3** was treated with the lithium salt of trimethylsilylacetylene (TMSA), compound **9** was obtained in 34% yield. The trimethylsilyl group of **9** was removed with a 0.1 N solution of NaOH in methanol[19] to give the ethynyl selenide **2** in 76% yield.

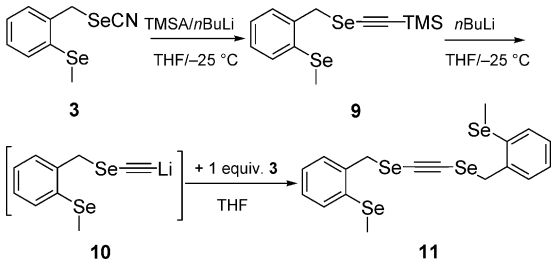


Scheme 1. Synthesis of methyl (methylselenyl)benzyl selenides **1**, **14**, and **15**.



Scheme 2. Stepwise procedure for the synthesis of model compounds **2** and **3**.

When we tried to use *n*BuLi as the deprotonation agent for TMSA in the presence of **3** to generate **9**, we observed compound **11** as a side-product (Scheme 3). We assume that **11** was generated by the reaction of the lithium salt **10** with **3**. The disubstituted alkyne turned out to be a solid, the molecular structure of which could be studied (see below).



Scheme 3. Probable side-reaction sequence leading to the formation of **11**.

The *meta* and *para* isomers of **1** (**14** and **15**) and benzyl ethynyl selenide (**17**) were also synthesized as model systems by using methods analogous to those shown in Schemes 1 and 2 (see the Exp. Sect.).

X-ray Investigations

We were able to grow single crystals of **3** and **11** that were suitable for X-ray diffraction studies. In Figure 2 we show the molecular structure of **3**, which forms a dimeric aggregate in the solid state. The intermolecular interactions between the selenium centers of **3** are short (347 pm) and are among the shortest Se···Se van der Waals distances reported in the literature. Only 15 out of the 227 compounds, for which distances below 380 pm (representing the sum of the van der Waals radii of the two Se centers) are reported in the Cambridge Crystallographic Database,[20] have Se···Se distances equal to or below 347 pm. Both of the Se1···Se2–CN and Se2···Se1–C_{arom} moieties are nearly linear.

In **3** we also encounter an intramolecular Se···Se contact of 372 pm, which is less than the sum of the van der Waals radii of two Se centers.[21] Furthermore, the distance between Se1 and one benzylic hydrogen atom is short (275 pm), which indicates weak hydrogen bonding.[22] In the solid state the dimers of **3** build a two-dimensional net, forming N···Se intermolecular interactions between the nitrogen atoms of the CN groups and the selenium atoms of a neighboring pair (Figure 3). The Se···N distance of 313 pm is relatively short compared with the sum of the van der Waals radii of nitrogen and selenium (345 pm).[21] The N···Se–C angle is 166.7°, which provides the possibility of an n(sp)–σ* interaction between the lone pair of the nitrogen atom and the C–Se σ* orbital.

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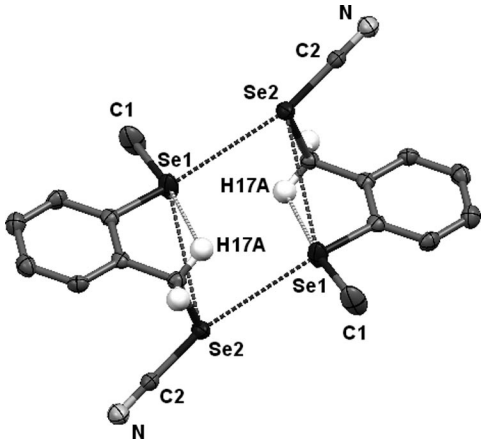

Figure 2. Molecular structure of the dimeric structure of **3** in the solid state. Dark-grey dotted lines represent intermolecular Se···Se (347 pm) and intramolecular Se···Se (372 pm) interactions. Light-grey dotted lines illustrate intramolecular Se–H interactions (275 pm). The hydrogen atoms on the phenyl rings have been omitted for the sake of clarity.

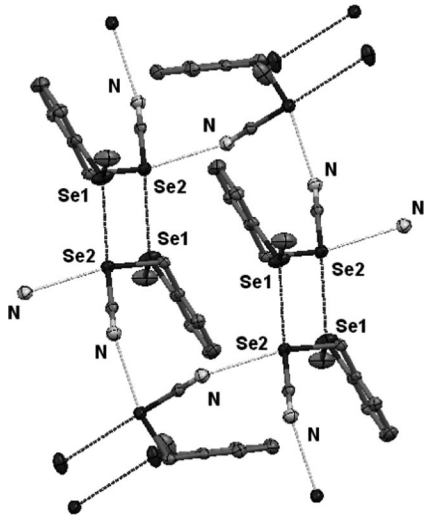

Figure 3. Two-dimensional net of **3** in the solid state. The Se···Se (dark-grey) and Se···N (light-grey) interactions are indicated with dotted lines. Hydrogen atoms have been omitted for the sake of clarity.

We also studied the structure of the side-product **11**, especially after finding out that **2** could not be crystallized. Thus, we were able to investigate the structural properties of a molecule closely related to **2**. The molecular structure of **11** is depicted in Figure 4.

We encounter in this structure strong intramolecular interactions between the Se1 and Se2 centers. The Se1···Se2 distance is 364 pm, which is shorter than the intramolecular Se···Se interaction in **3** (372 pm). Also surprising is the short Se···H contact between Se1 and the benzylic proton. Its value (277 pm) is well below the sum of the van der Waals radii (310 pm)[21] and also shorter than the first reported Se···H contact.[23]

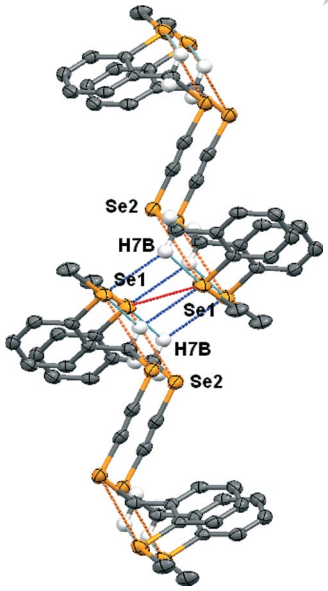

Figure 4. Structure of **11** in the solid state. The two-dimensional structure is a result of the intermolecular Se···Se (red) and Se···H interactions (blue). Intramolecular Se···Se (dark-orange) and Se···H (light-grey) interactions are also depicted. For the sake of clarity only selected hydrogen atoms are shown.

NMR Investigations

Various groups have utilized ^{77}Se NMR chemical shifts to study the interactions of divalent Se centers with other atoms such as halogen or chalcogen centers. It was found that the ^{77}Se NMR chemical shift (δ_{Se}) is sensitive to the environment around the Se center, and its shift can be used as a measure of the strength of the nonbonding interactions of Se with other atoms with lone pairs.[24–26] To explore whether there are intramolecular nonbonding interactions between the Se centers of **1**–**3** in solution, first we compared the ^{77}Se NMR chemical shifts of **1** with the model compounds **12**–**16** shown in Figure 5.

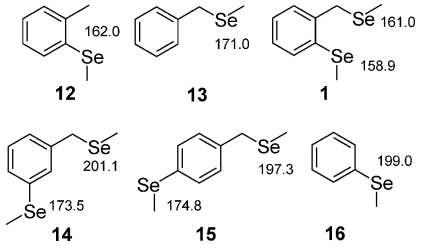

Figure 5. Model systems **1** and **12**–**16** with the ^{77}Se NMR chemical shifts.

Originally we thought that methyl phenyl selenide (**16**) (δ_{Se} = 199 ppm)[26] might be a good model for **1**. However, comparison of its δ_{Se} value with that obtained for **12** shows that the latter is better suited for our purpose. The methyl group in the *ortho* position to the $SeCH_3$ substituent leads to a high-field shift of 37 ppm due to the γ effect on the ^{77}Se chemical shifts.[27] We also compared the ^{77}Se chemical

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shift of the isomers **1**, **13**, **14**, and **15** to check if the observed chemical shifts are not simply due to substitution at different positions of the aromatic ring. The introduction of another selenium-containing substituent at the *meta* (**14**) or *para* position (**15**) of **13** causes a deshielding of the Se center from 171 (**13**) to 201 (**14**) and 197 ppm (**15**), whereas for the *ortho* position (**1**) a significant shielding effect (161 pm) was detected. If we compare the δ_{Se} values for the $SeCH_3$ groups, we observe a shielding of around 25 ppm for the compounds **14** and **15** in comparison with **16**. An even stronger shielding of 40 ppm is encountered in the case of **1**. We interpret the strong upfield shifts for the two Se nuclei of **1** just discussed as being a result of a Se···Se interaction.

In Figure 6 we have listed the ^{77}Se chemical shifts of **1**–**3**, **13**, and **17**–**21**. Comparison of the δ_{Se} values for **12** (δ = 162 ppm), **1** (δ = 159 ppm), **2** (δ = 158 ppm), and **3** (δ = 157 ppm) reveals for the Se–CH_3 group a high-field shift for **1**–**3**, which supports increased electron density around the Se atom bound to the methyl group.

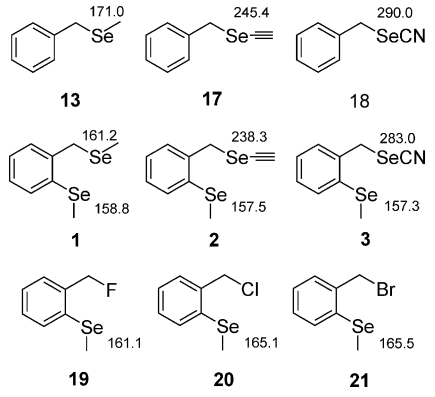

Figure 6. Comparison of ^{77}Se chemical shifts of **1**–**3** with **13** and **17**–**21**.

Comparison of the δ_{Se} values for **13** (δ = 171 ppm) and **1** (δ = 161 ppm), **17** (δ = 245 ppm) and **2** (δ = 238 ppm), and **18** (δ = 290 ppm) and **3** (δ = 283 ppm) also reveals a high-field shift of the second Se-containing group in **1**–**3**. This indicates that despite the electron-withdrawing nature of the C≡CH and CN groups, there is also increased electron density on the second Se atom.

Taking the results together, it can be concluded that there is increased electron density around both Se atoms in **1**–**3**. The data are best understood on the basis of van der Waals interactions rather than p–σ* interactions between the Se centers. A comparison with the literature data reported for **19**–**21**[24c] (Figure 6) leads us to assume that the Se···Se interaction is slightly stronger than the Se–halogen interaction.

Comparison of the ^1H and ^{13}C NMR chemical shifts of the methyl groups in **1**–**3** (Table 1) shows a downfield shift in the series compared with **16**, whereas the δ_{Se} values are shifted upfield, which suggests that electron density is transferred from the CH_3 group to the Se atom.

Table 1. Selected ^1H, ^{13}C, and ^{77}Se NMR chemical shifts [ppm] for **1**–**3** and **16** in CD_2Cl_2.

Compound	δ_H CH_3	δ_C CH_3	δ_{Se} $SeCH_3$	δ_{Se} SeX
16	2.30	7.2	199	–
1	2.33	7.7	158.9	161.0
2	2.35	8.3	157.5	238.6
3	2.37	9.0	157.3	283.0

An even more sensitive probe for our investigations was the coupling constant between the interacting Se atoms in **1**–**3**. Although the chemical shift is indicative of the local electron environment, the *J* coupling provides a direct spectral manifestation of the chemical bonding.[28] Two nuclear spins show a measurable *J* coupling only if they are linked together through chemical bonds. A careful examination of the satellites of the ^{77}Se signals in the NMR spectra of **1**–**3** allowed us to determine the long-range coupling between the two selenium atoms. For **1**, the ^{77}Se NMR spectrum showed relatively broad signals for both peaks, which suggests the existence of several conformers in solution. To determine the coupling constant for **1**, a 2D homonuclear ^{77}Se–^{77}Se shift correlation experiment with proton decoupling was performed.[29] These measurements yielded $^4J_{Se,Se}$ = 37.8 (**1**), 40.9 (**2**), and 58.8 Hz (**3**). The increase in the coupling constant across the series **1**, **2**, and **3** indicates an increase in the spin interaction between the two selenium nuclei, which is indicative of a growth in the intramolecular Se···Se interaction. Confirming these suppositions, the long-range $^4J_{Se,Se}$ coupling for 2-(cyanoselenyl)benzyl selenocyanate (**22**) was determined to be 34 Hz, which illustrates that for the case, in which the substituents on the two selenium centers are electron-withdrawing groups, the Se···Se interaction is less favored. From this result and the fact that $^4J_{Se,Se}$ increases from **1** to **2** to **3**, it can be deduced that besides the van der Waals bonding the p–σ* interaction between the two Se centers also plays a role.

To assess the $^4J_{Se,Se}$ values recorded for **1**–**3**, we compared them with the values obtained for cyclic systems, for which no van der Waals contacts have been reported. In selenium sulfide rings, the values for $^4J_{Se,Se}$ vary between 0.5 and 19 Hz.[30] In systems such as 1,8-bis(selanyl)naphthalene derivatives, in which both Se centers are forced into close proximity, considerably larger values of $^4J_{Se,Se}$ have been reported.[31]

Conformational Analysis of 1–3

The geometrical parameters of **1**–**3** were optimized by density functional theory (DFT)[32] using Becke's three-parameter hybrid functional[33] combined with the Lee–Yang–Parr correlation functional (B3LYP).[34] We used a basis set from Pople/McLean–Chandler's 6-311G family[35] with polarization and diffuse functions as implemented in the Gaussian 03 software.[36] The preliminary geometries obtained were refined by utilizing Becke's B98 hybrid functional.[37] The optimized geometries obtained by the described protocol were used to determine the energies using

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the MP2 method.[38] Thus, the energies given for **1**–**3** were obtained at the MP2/6-311+G(d)//B98/6-311+G(d) level of theory.

For **1**–**3** we found four conformers that are very close in energy. We labeled them as $(endo/exo)_{H/X}$ in which *endo*/*exo* refers to the position of the substituent on the Se–X group with respect to the benzene ring and H/X refers to the most significant intramolecular interaction observed.

In Figure 7 we show the four lowest-energy conformations of **1**–**3**, together with the most pronounced interactions, indicated by dotted lines. Their energies and the most pronounced interactions, that is, the intramolecular Se···Se and C–H···Se interactions are listed in Table 2. The $endo_H$ and exo_H conformations are marked by two Se···H distances, which vary between 278 and 336 pm. The Se···Se distances in these conformations are usually longer than in the $endo_X$ and exo_X conformations.

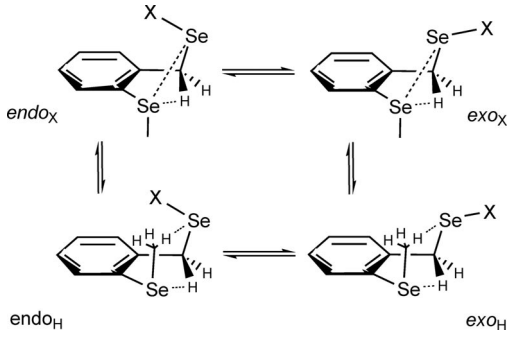

Figure 7. Equilibrium between all four conformers of compounds **1**–**3**, with the definition of the *exo*/*endo* and H/X terms. The most important intermolecular interactions are depicted by dotted lines.

Table 2. Relative energies and the main Se···Se and H···Se interactions of the four conformations $endo_H/exo_H$ and $endo_X/exo_X$ of **1**–**3**.[a]

Compound		Relative energy [kcal/mol]	Se···Se [pm]	Se···H [pm]
1	$endo_H$	0.02	401	289, 317
	$endo_X$	0.00	371	290
	exo_H	1.09	434	278, 316
	exo_X	1.41	381	282
2	$endo_H$	0.00	390	289, 326
	$endo_X$	0.47	382	288
	exo_H	1.27	433	278, 316
	exo_X	1.76	388	279
3	$endo_H$	0.00	380	292, 336
	$endo_X$	0.50	386	288
	exo_H	1.76	430	279, 327
	exo_X	2.09	389	278

[a] For the definitions of *endo*/*exo* and X/H, see Figure 7.

The $endo_X$ and exo_X conformations are characterized by only one weak Se···H interaction, which varies between 278 and 290 pm, and a relatively short Se···Se distance varying between 370 and 388 pm. Although the energy differences between the four conformers of **1**–**3** are very small, we can conclude that Se···H interactions, beside Se···Se interactions, play an important part in stabilizing the conformations in solution.

Calculations of the ^{77}Se NMR Shifts of 1–3

We used DFT methods to find the optimum procedure for calculating the ^{77}Se chemical shifts of **1**–**3** due to the size of the molecules. A number of model calculations on small molecules such as HSeH, CH_3SeCH_3, SeCO, CSe_2, and CH_3SeH showed that the gauge-independent atomic orbital (GIAO)[39] method using Becke's B98 functional[37] as well as the hybrid functional of Perdew–Burke–Ernzerhof (PBE)[40] with the TVZP basis set of Ahlrichs[41] performed very well in calculations of the ^{77}Se NMR magnetic shieldings. This impression was underpinned when we calculated the ^{77}Se chemical shifts of **13**, **17**, and **18**. In Table 3 we list the ^{77}Se chemical shifts obtained for the $SeCH_3$ (a) and CH_2–Se–X (b) centers by utilizing the geometrical parameters obtained at the B98/6-311+G(d) level of theory. The chemical shifts were obtained from the calculated isotropic magnetic shieldings of compounds **1**–**3** (listed in the Supporting Information), referenced to the isotropic magnetic shieldings calculated for dimethyl selenide at the same computational level.

Table 3. Calculated chemical shifts [ppm] for each of the four conformers (see Figure 7) of compounds **1**–**3** by using the optimized geometries calculated at the B98 level of theory. The conformation agreeing best with the experimental results (cf. Table 1) is indicated in italics.

Compound		GIAO-B98		GIAO-PBE	
		$SeCH_3$ (a)	CH_2–Se–X (b)	$SeCH_3$ (a)	CH_2–Se–X (b)
1	$endo_H$	217.0	129.5	215.6	129.5
	$endo_X$	192.4	119.4	191.5	122.7
	exo_H	*162.1*	*148.0*	*161.3*	*146.7*
	exo_X	135.0	125.8	134.8	128.6
2	$endo_H$	*116.8*	*236.9*	*116.7*	*236.2*
	$endo_X$	110.5	258.9	110.4	258.2
	exo_H	152.2	154.5	150.6	156.9
	exo_X	127.5	133.5	130.3	136.9
3	$endo_H$	*107.1*	*277.9*	*108.0*	*275.1*
	$endo_X$	*111.3*	*294.9*	*111.0*	*292.4*
	exo_H	150.8	165.0	149.2	167.3
	exo_X	141.5	141.3	145.3	143.4

For all four conformers of **1**, an upfield shift of the chemical shift for the ^{77}Se nuclei was predicted relative to those of **13** and **16**. The best agreement between calculated and experimental values [δ =158.9 ppm for Se (b) and 161 ppm for Se (a)] was obtained for the exo_H conformer by both methods.

In the case of **2** the best agreement between calculation and experiment [δ =238.3 ppm for Se (b) and 157.5 ppm for Se (a)] was found for the $endo_H$ conformer, which also

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represents the most stable conformer. Again a high-field shift was predicted relative to the Se centers of **16** and **17**.

For **3** the values predicted for the *endo*$_X$ and *endo*$_H$ conformers agree best with the recorded chemical shifts [δ = 283.0 ppm for Se (b) and 157.3 ppm for Se (a)]. Note that the solid-state structure of **3** shows a conformation between *endo*$_X$ and *endo*$_H$.

Conclusions

The three model systems **1**–**3** provide two selenium centers in close proximity with the possibility of close Se···Se contacts. In the cases of **3** and **11**, a derivative of **2**, we found close Se···Se contacts in the solid state. Our study of the ^{77}Se NMR chemical shifts of **1**–**3** provided evidence for an increase of electron density around both Se centers. This observation was underpinned by the coupling constants $^4J_{Se,Se}$, which increased from **1** to **3**. These results are supported by model calculations. The calculations of the ^{77}Se NMR chemical shifts agree best with the experimental results when we assume conformations, in which the Se···Se and Se···H–C interactions prevail. The ^{77}Se chemical shift data and the $^4J_{Se,Se}$ coupling constants indicate that the Se···Se interactions are mainly due to van der Waals-type bonding rather than p–σ* interactions.

Table 4. Crystal data and structural refinement for **3** and **11**.

	3	**11**
Empirical formula	$C_9H_9NSe_2$	$C_{18}H_{18}Se_4$
Formula mass	289.09	550.16
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
Z	4	4
a [Å]	8.8538(1)	15.856(2)
b [Å]	16.6622(4)	5.2497(7)
c [Å]	7.2143(2)	22.816(3)
β [°]	113.004(1)	101.456(3)
V [Å^3]	979.65(4)	1861.4(4)
$D_{calcd.}$ [g/cm^3]	1.96	1.96
μ [mm]$^{-1}$	7.49	7.88
Crystal shape	polyhedron	polyhedron
Crystal size [mm]	0.26 × 0.14 × 0.04	0.35 × 0.06 × 0.04
Crystal color	pale yellow	colorless
θ range [°]	2.4–27.5	1.8–26.1
Index ranges	$-11 \le h \le 11$	$-19 \le h \le 19$
	$-21 \le k \le 21$	$-6 \le k \le 6$
	$-9 \le l \le 9$	$-28 \le l \le 28$
Reflections collected	10108	7851
Independent reflections [R(int)]	2259 [0.0602]	1846 [0.0422]
Observed reflections	1723 [$I > 2\sigma(I)$]	1486 [$I > 2\sigma(I)$]
Max./min. transmission	0.75/0.25	0.74/0.17
Data/restraints/parameters	2259/0/110	1846/0/101
Goodness-of-fit on F^2	1.02	1.04
$R(F)$	0.031	0.033
$R_w(F^2)$	0.065	0.074
$\Delta p_{max.}/\Delta p_{min.}$ [e Å^{-3}]	0.75/–0.84	0.72/–0.45

Experimental Section

General Remarks: All melting points are uncorrected and were measured in an open capillary by using a Dr. Tottoli melting point apparatus from Büchi, Swiss Company. The NMR spectra were measured with Bruker ARX500 (^{1}H NMR at 500 MHz, ^{13}C NMR at 125 MHz, and ^{77}Se NMR at 95 MHz) and ARX300 spectrometers (^{1}H NMR at 300 MHz and ^{13}C NMR at 75 MHz) by using the solvent as reference for ^{1}H NMR spectra and the XSI scale for the heteronuclei. Heteronuclear J couplings involving Se have been determined by inspection of satellites of proton and carbon signals, respectively, in the corresponding spectra (see also Supporting Information). High-resolution mass spectra (HRMS) were obtained with ZAB-3F (Vacuum Generators) and JEOL JMS 700 high-resolution mass spectrometers. UV/Vis absorption spectra were recorded with a Hewlett–Packard HP 8452A diode-array spectrometer. IR spectra were recorded with a Bruker Vector 22 FTIR spectrometer. All reactions were carried out in dry degassed solvents under argon, unless otherwise stated.

X-ray Crystallographic Study: The data were collected with Bruker Smart CCD (**3**) and APEX diffractometers (**11**) at 200 K by using Mo-K_α radiation (0.71073 Å). Selected crystal data and data-collection parameters for **3** and **11** are given in Table 4. In both cases, the collection strategies used ω-scans (0.3°) covering a whole sphere in the reciprocal space, intensities were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied by using SADABS[42] based on the Laue symmetry of the reciprocal space. The structures were solved by direct methods and refined against F^2 by using the SHELXTL (5.10) software package.[43] CCDC-718378 (**3**) and -718379 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for the Synthesis of Lithium Methaneselenolate: Methyllithium (commercial solution, 1.6 M in diethyl ether, 30 mL, 45 mmol) was added dropwise by using a syringe to a stirred suspension of gray selenium powder (3.2 g, 40 mmol) in THF (50 mL), cooled to –25 °C under argon. After complete addition of the MeLi solution under continuous stirring, the reaction mixture was warmed to room temperature for 2 h. On reaching room temperature, full consumption of the selenium powder could be observed.

General Procedure for the Synthesis of Methyl (Methylselenyl)benzyl Selenides 1, 14, and 15: A solution of the corresponding bromobenzyl bromide **4a**–**c** in freshly distilled DMF (ca. 50 mL) was added dropwise by syringe, whilst stirring, to a solution of lithium methaneselenolate in THF (freshly prepared as described above). The reaction flask, a four-necked round-bottomed flask, was immersed in a silicon bath, and the THF and diethyl ether were distilled off. Then the flask was fitted with a reflux condenser, and the reaction mixture was heated under reflux at 135 °C for more than 48 h. After heating at reflux, the alkylating agent methyl iodide was added, whilst stirring, and the reaction mixture was cooled to room temp. The reaction mixture was quenched by adding it dropwise to deionized water (50 mL) and extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with water and brine and dried with $MgSO_4$. The solvent was removed by rotary evaporation usually to afford a dark-reddish oil. Pure products were obtained after purification by silica gel column chromatography.

Methyl 2-(Methylselenyl)benzyl Selenide (1): Starting materials: 2-bromobenzyl bromide (**4a**; 2.5 g, 10 mmol), freshly prepared lithium methaneselenolate (4.0 g, 40 mmol in 80 mL THF/diethyl ether solution), and methyl iodide (2.5 mL, 40 mmol). Reaction time: 54 h. Gradient chromatography on silica gel by using light petroleum/diethyl ether (20:1 to 10:1) afforded 0.7 g (25%) of pure **1** as

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a yellow oil. MS (EI): *m*/*z* (%) = 280 (42.5) $[M]^+$, 265 (62.1) $[M - CH_3]^+$, 250 (40.6) $[M - 2CH_3]^+$, 185 (37.4) $[M - SeCH_3]^+$, 169 (53.9) $[C_7H_7Se]^+$, 105 (100) $[C_8H_9]^+$, 91 (43.8) $[C_7H_7]^+$, 78 (11.5) $[C_6H_5]^+$. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.93 (s, $^2J_{Se,H}$ = 10.6 Hz, 3 H, CH_2SeCH_3), 2.32 (s, $^2J_{Se,H}$ = 11.8 Hz, 3 H, CH_3), 3.87 (s, $^2J_{Se,H}$ = 12.6 Hz, 2 H, CH_2), 7.13–7.18 (m, 3 H, H_{arom}) [at low temperature it separated into three signals: δ = 7.25 (ddd, *J* = 7.8, 7.5, 1.5 Hz, 1 H), 7.16 (ddd, *J* = 7.8, 7.6, 1.2 Hz, 1 H), 7.09 (dd, *J* = 7.5, 1.2 Hz, 1 H)], 7.41 (dd, *J* = 7.6, 1.5 Hz 1 H, H_{arom}) ppm. ^{13}C NMR (125MHz, CD_2Cl_2): δ = 4.6 (p-CH_2SeCH_3, $^1J_{Se,C}$ = 64.6 Hz), 7.6 (p-$SeCH_3$, $^1J_{Se,C}$ = 65.1 Hz), 28.9 (s-CH_2Se, $^1J_{Se,C}$ = 57.9, $^3J_{Se,C}$ = 13.0 Hz), 126.2 (t-C_{arom}), 127.8 (t-C_{arom}), 129.8 (t-C_{arom}), 131.0 (t-C_{arom}), 133.4 (q-C_{arom}, C-Se), 140.1 (q-C_{arom}, C-CH_2) ppm. ^{77}Se NMR (95 MHz, CD_2Cl_2): δ = 158.9 ($^4J_{Se,Se}$ = 37.8 Hz, $SeCH_3$), 161.0 ($^4J_{Se,Se}$ = 37.8 Hz, CH_2SeCH_3) ppm. IR (film): $\tilde{\nu}$ = 3055 (w), 3001 (m), 2923 (s), 2072 (w), 1948 (w), 1692 (w), 1583 (m), 1463 (s), 1438 (s), 1424 (s), 1270 (m), 1031 (m), 904 (m), 754 (vs) cm^{-1}. HRMS (positive EI): calcd. for $^{12}C_9{}^1H_{12}{}^{78}Se^{82}Se$ $[M]^+$ 279.9269; found 279.9287 (+0.8 mmu).

Methyl 3-(Methylselenyl)benzyl Selenide (14): Starting materials: 3-bromobenzyl bromide (**4b**; 5.0 g, 20 mmol), freshly prepared lithium methaneselenolate (10.1 g, 100 mmol, in 200 mL THF/diethyl ether solution), and methyl iodide (6.25 mL, 100 mmol). Reaction time: 66 h. Column chromatography on silica gel by using light petroleum/diethyl ether (10:1) afforded 0.7 g (13%) of pure **14** as a yellow oil. MS (EI): *m*/*z* (%) = 280 (24.2) $[M]^+$, 265 (0.5) $[M - CH_3]^+$, 249 (0.9) $[M - 2CH_3]^+$, 185 (100) $[M - SeCH_3]^+$, 170 (31.3) $[C_7H_7Se]^+$, 104 (32.5) $[C_8H_9]^+$, 95 (7) $[CH_3Se]^+$, 91 (8.9) $[C_7H_7]^+$, 78 (5.9) $[C_6H_5]^+$. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.91 (s, $^2J_{Se,H}$ = 10.6 Hz, 3 H, CH_3), 2.34 (s, $^2J_{Se,H}$ = 11.2 Hz, 3 H, CH_3), 3.69 (s, $^2J_{Se,H}$ = 13.3 Hz, 2 H, CH_2), 7.094 (dt, *J* = 7.6, 1.3 Hz, 1 H, H_{arom}), 7.18 (t, *J* = 7.6 Hz, 1 H, H_{arom}), 7.25 (dt, *J* = 7.6, 1.3 Hz, 1 H, H_{arom}), 7.31 (t, *J* = 1.3 Hz, 1 H, H_{arom}) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 4.4 (p-CH_2SeCH_3), 7.1 (p-$SeCH_3$), 28.2 (s-CH_2Se), 126.9 (t-C_{arom}), 128.5 (t-C_{arom}), 129.3 (t-C_{arom}), 130.6 (t-C_{arom}), 132.4 (q-C_{arom}, C-CH_2), 140.9 (q-C_{arom}, C-Se) ppm. ^{77}Se NMR (95 MHz, CD_2Cl_2): δ = 173.5 ($SeCH_3$), 201.1 (CH_2SeCH_3) ppm. IR (film): $\tilde{\nu}$ = 3049 (w), 3000 (m), 2923 (s), 2253 (w), 1598 (s), 1568 (s), 1474 (s), 1423 (s), 1272 (m), 1185 (w), 1074 (m), 903 (m), 782 (s), 696 (vs) cm^{-1}. HRMS (positive EI): calcd. for $^{12}C_9{}^1H_{12}{}^{78}Se^{80}Se$ $[M]^+$ 279.9277; found 279.9272 (–0.5 mmu).

Methyl 4-(Methylselenyl)benzyl Selenide (15): Starting materials: 4-bromobenzyl bromide (**4c**; 2.5 g, 10 mmol), freshly prepared lithium methaneselenolate (4.0 g, 40 mmol, in 80 mL THF/diethyl ether solution), and methyl iodide (2.5 mL, 40 mmol). Reaction time: 60 h. Column chromatography on silica gel by using light petroleum/diethyl ether (100:1) afforded 0.58 g (21%) of pure **15** as yellow oil. MS (EI): *m*/*z* (%) = 280 (14.5) $[M]^+$, 265 (1.1) $[M - CH_3]^+$, 249 (0.6) $[M - 2\ CH_3]^+$, 185 (100) $[M - SeCH_3]^+$, 170 (61.6) $[C_7H_7Se]^+$, 104 (12) $[C_8H_9]^+$, 95 (3.7) $[CH_3Se]^+$, 91 (4.8) $[C_7H_7]^+$, 78 (15) $[C_6H_5]^+$. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.90 (s, $^2J_{Se,H}$ = 10.6 Hz, 3 H, CH_3), 2.33 (s, $^2J_{Se,H}$ = 11.1 Hz, 3 H, CH_3), 3.69 (s, $^2J_{Se,H}$ = 14.4 Hz, 2 H, CH_2), 7.16 (ddd, *J* = 8.4, 2.1, 0.9 Hz, 2 H, H_{arom}), 7.33 (ddd, *J* = 8.4, 2.1 Hz, 2 H, H_{arom}) ppm. ^{13}C NMR (125MHz, CD_2Cl_2): δ = 4.3 ($^1J_{Se,C}$ = 64.3 Hz, p-CH_2SeCH_3), 7.3 ($^1J_{Se,C}$ = 64.9 Hz, p-$SeCH_3$), 28.1 ($^1J_{Se,C}$ = 58.4 Hz, s-CH_2Se), 129.8 (t-C_{arom}), 130.3 (q-C_{arom}, C-CH_2), 130.6 ($^2J_{Se,C}$ = 11.5 Hz, t-C_{arom}), 138.0 (q-C_{arom}, C-Se) ppm. ^{77}Se NMR (95 MHz, CD_2Cl_2): δ = 174.8 ($SeCH_3$), 197.3 (CH_2SeCH_3) ppm. IR (film): $\tilde{\nu}$ = 3047 (w), 2999 (m), 2922 (s), 2226 (w), 1593 (w), 1489 (s), 1423 (m), 1398 (m), 1272 (m), 1070 (m), 905 (m), 826 (m) cm^{-1}. HRMS (positive EI): calcd. for $^{12}C_9{}^1H_{12}{}^{80}Se$ $[M]^+$ 279.9269; found 279.9254 (–1.6 mmu).

2-Bromobenzyl *tert*-Butyldimethylsilyl Ether (6): A solution of TBSCl (5.6 g, 37 mmol) in dry DMF (10 mL) was added by using a syringe to a solution of 2-bromobenzyl alcohol (**5**; 5.8 g, 31.0 mmol) and imidazole (5.2 g, 76.4 mmol) in dry DMF (50 mL) in a 250 mL Schlenk flask. The reaction mixture was stirred at room temperature for 20 h. The reaction was quenched with deionized water (100 mL) and extracted with diethyl ether (4 × 70 mL). The combined organic layers were washed with water and brine and then dried with $MgSO_4$. The solvent was evaporated to afford a brown oil as raw product. A yield of 8.6 g of **6** (92%) was isolated by purification using column chromatography on silica gel, eluting with petroleum ether/dichloromethane (10:1). MS (EI): *m*/*z* (%) = 301 (ca. 1) $[M]^+$, 243 (100) $[M - C_4H_9]^+$, 213 (27.2) $[M - C_6H_{15}]^+$, 169 (46.9) $[M - C_6H_{15}OSi]^+$, 105 (5.2) $[C_7H_6O]^+$, 90 (3.5) $[C_7H_6]^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.15 [s, 6 H, $Si(CH_3)_2$], 0.99 [s, 9 H, $SiC(CH_3)_3$], 4.76 (s, 2 H, CH_2), 7.12 (td, *J* = 7.8, 0.5 Hz, 1 H, H_{arom}), 7.34 (td, *J* = 7.8, 0.6 Hz, 1 H, H_{arom}), 7.50 (dd, *J* = 7.9, 0.5 Hz, 1 H, H_{arom}), 7.58 (dd, *J* = 7.8, 0.6 Hz, 1 H, H_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –5.3 [2 C, *p*-$Si(CH_3)_2$], 18.4 [q-$SiC(CH_3)_3$], 25.9 [3 C, *p*-$SiC(CH_3)_3$], 64.6 (s-CH_2), 121.0 (q-C_{arom}Br), 127.3 (t-C_{arom}), 127.5 (t-C_{arom}), 128.1 (t-C_{arom}), 132.0 (t-C_{arom}), 140.3 (q-$C_{arom}CH_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3500–3150 (br. s), 2955 (s), 2930 (s), 2885 (m), 2857 (s), 1700 (m), 1471 (m), 1442 (m), 1291 (s), 1255 (m), 1201 (m), 1130 (m), 1098 (m), 1044 (m), 1027 (m) cm^{-1}.

***tert*-Butyldimethylsilyl 2-(Methylselenyl)benzyl Ether (7):** A solution of lithium methaneselenolate (6.0 g, 60 mmol) in THF/diethyl ether solution (100 mL, prepared as described above) was added to a solution of **6** (6.03 g, 20 mmol) in dry DMF (100 mL). The reaction mixture was heated to 70 °C to remove the THF and diethyl ether by distillation. Subsequently, the reaction solution was heated at 80–90 °C under vigorous stirring for a further 60 h. After cooling to room temperature, the alkylating agent MeI (3.8 mL, 60 mmol) was added and stirring continued for 45 min. Then the reaction was quenched with water (ca. 200 mL). After extraction with diethyl ether (4 × 100mL), the combined organic layers were washed with water, a saturated $NaHCO_3$ solution, and brine, and then dried with $MgSO_4$. After removal of the solvent, the raw product was obtained as an orange oil. A yield of 2.98 g of pure **7** (47%) was isolated by column chromatography on silica gel, eluting with petroleum ether (b.p. 30–40 °C)/diethyl ether (10:1), as a dark-yellow oil. MS (EI): *m*/*z* (%) = 316 (>1) $[M]^+$, 259 (100) $[M - C_4H_9]^+$, 185 (50.7) $[M - C_6H_{15}SiO]^+$, 169 (12.0) $[M - C_7H_{18}SiO]^+$, 91 (27.2) $[M - C_7H_{18}SiOSe]^+$, 105 (49.3) $[C_7H_5O]^+$. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.12 [s, 6 H, $Si(CH_3)_2$], 0.95 [s, 9 H, $SiC(CH_3)_3$], 2.30 (s, 3 H, $SeCH_3$), 4.74 (s, 2 H, CH_2), 7.19 (td, *J* = 7.4, 1.3 Hz, 1 H, H_{arom}), 7.22 (td, *J* = 7.4, 0.5 Hz, 1 H, H_{arom}), 7.37 (dd, *J* = 7.4, 1.3 Hz, 1 H, H_{arom}), 7.42 (td, *J* = 7.4, 0.5 Hz, 1 H, H_{arom}) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = –5.2 [2 C, p-$Si(CH_3)_2$], 7.0 (p-$SeCH_3$), 18.7 [q-$SiC(CH_3)_3$], 26.1 [3 C, p-$SiC(CH_3)_3$], 65.0 (s-CH_2), 126.3 (t-C_{arom}), 127.2 (t-C_{arom}), 128.0 (t-C_{arom}), 129.8 (t-C_{arom}), 131.3 (q-$C_{arom}SeCH_3$), 141.5 (q-$C_{arom}CH_2$) ppm. ^{77}Se NMR (95 MHz, CD_2Cl_2): δ = 154.5 ppm. IR (film): $\tilde{\nu}$ = 3059 (w), 2954 (s), 2929 (s), 2885 (m), 2856 (s), 1467 (m), 1448 (m), 1255 (s), 1201 (m), 1123 (m), 1093 (s), 1051 (m), 1034 (m) cm^{-1}. HRMS (positive EI): calcd. for $^{12}C_{14}{}^1H_{24}{}^{16}O^{28}Si^{80}Se$ $[M]^+$ 316.0762; found 316.0760 (–0.1 mmu).

2-(Methylselenyl)benzyl Alcohol (8): Compound **7** (5.7 g, 18 mmol) was added to a solution of acetic acid (103 mL), THF (34 mL), and water (34 mL). The slightly pale mixture was stirred at room temperature for 20 h. After extraction with diethyl ether (4 × 100 mL), the combined organic layers were washed with a large quantity of water and then saturated $NaHCO_3$ solution and

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brine. The organic layers were dried with $MgSO_4$, and then the solvent was removed by rotary evaporation. The raw product was purified by column chromatography on deactivated silica gel, eluting with petroleum ether (b.p. 30–40 °C)/dichloromethane (1:1), which resulted in 3.36 g of compound **8** (93%) as a light-colored oil. MS (EI): *m*/*z* (%) = 202 (61.0) $[M]^+$, 187 (36.6) $[M - CH_3]^+$, 157 (28.0) $[M - C_2H_5O]^+$, 105 (95.1) $[C_7H_5O]^+$, 77 (100) $[C_6H_5]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.19 (s, 1 H, OH), 2.33 (s, $^2J_{Se,H}$ = 11.6 Hz, 3 H, $SeCH_3$), 4.74 (s, 2 H, CH_2), 7.22–7.26 (m, 2 H, H_{arom}), 7.36–7.38 (m, 1 H, H_{arom}), 7.42–7.44 (m, 1 H, H_{arom}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 7.4 (p-$SeCH_3$), 65.1 (s-CH_2), 126.6 (t-C_{arom}), 128.1 (t-C_{arom}), 128.4 (t-C_{arom}), 130.7 (t-C_{arom}), 131.5 (q-$C_{arom}SeCH_3$), 140.9 (q-$C_{arom}CH_2$) ppm. ^{77}Se NMR (95 MHz, $CDCl_3$): δ = 155.1 ppm. IR (film): $\tilde{\nu}$ = 3348 (br. s), 3057 (m), 2927 (m), 1587 (w), 1464 (m), 1442 (s), 1428 (s), 1197 (m), 1060 (m), 1028 (s), 908 (m), 749 (vs) cm^{-1}. HRMS (positive EI): calcd. for $^{12}C_8{}^1H_{10}{}^{16}O^{80}Se$ $[M^+]$ 201.9897; found 201.9891 (–0.6 mmu).

2-(Methylselenyl)benzyl Selenocyanate (3): To synthesize selenocyanogen, KSeCN (4.2 g, 29.0 mmol) was dissolved in THF (200 mL) and placed in a 500 mL three-necked flask. After cooling to –15 °C, bromine (0.75 mL, 14.6 mmol) was added by syringe through a rubber lid. An orange color appeared that turned deep-yellow by the end of the addition process. The mixture was cooled to –78 °C, stirred for 45 min, and filtered through a glass frit (under vacuum) into a 1000 mL three-necked flask already cooled to –78 °C. Triphenylphosphane (3.8 g, 7.2 mmol), dissolved in anhydrous CH_2Cl_2 (200 mL), was added dropwise from a cooled dropping funnel, taking care that the reaction mixture did not rise above –65 °C during the addition procedure. The color turned to dark-orange during the addition. Afterwards, **8** (1.41 g, 7.0 mmol), dissolved in CH_2Cl_2 (50 mL), was slowly added by syringe in a controlled manner so that the reaction temperature would not exceed –70 °C. Following the complete addition, the reaction mixture was cooled to –78 °C and stirred overnight. After warming to room temperature, the reaction mixture was filtered and the solvent evaporated. The raw product was purified by column chromatography on deactivated silica gel with a mixture of petroleum ether (b.p. 30–40 °C)/CH_2Cl_2 (1:1) as eluent to afford 534 mg (26%) of **3** as pale-yellow crystals. MS (EI): *m*/*z* (%) = 291 (3.7) $[M]^+$, 185 (45.7) $[M - SeCN]^+$, 169 (23.0) $[M - CH_3SeCN]^+$, 105 (100) $[SeCN]^+$, 91 (48.1) $[C_7H_7]^+$. ^1H NMR (500 MHz, CD_2Cl_2): δ = 2.37 (s, $^2J_{Se,H}$ = 11.4 Hz, 3 H, $SeCH_3$), 4.40 (s, $^2J_{Se,H}$ = 15.2 Hz, 2 H, CH_2), 7.25 (td, *J* = 7.4, 1.6 Hz, 1 H, H_{arom}), 7.27 (td, *J* = 7.4, 2.0 Hz, 1 H, H_{arom}), 7.35 (dd, *J* = 7.4, 2.0 Hz, 1 H, H_{arom}), 7.52 (dd, *J* = 7.4, 1.6 Hz, 1 H, H_{arom}) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 9.0 (p-$SeCH_3$), 34.4 (s-CH_2), 102.6 (q-SeCN), 127.6 (t-C_{arom}), 129.8 (t-C_{arom}), 130.1 (t-C_{arom}), 132.8 (t-C_{arom}), 133.5 (q-$C_{arom}SeCH_3$), 137.7 (q-$C_{arom}CH_2$) ppm. ^{77}Se NMR (95 MHz, CD_2Cl_2): δ = 157.3 ($^4J_{Se,Se}$ = 58.8 Hz, $SeCH_3$), 283.0 ($^4J_{Se,Se}$ = 58.8 Hz, SeCN) ppm. IR (KBr): $\tilde{\nu}$ = 3424 (br. m), 3060 (w), 2992 (w), 2925 (m), 2153 (s), 1473 (m), 1462 (s), 1440 (m), 1420 (s), 1209 (m), 1187 (m), 1029 (s), 916 (m), 765 (s) cm^{-1}. HRMS (positive EI): calcd. for $^{12}C_9{}^1H_9{}^{14}N^{78}Se^{80}Se$ $[M]^+$ 290.9065; found 290.9080 (+0.5 mmu).

2-(Methylselenyl)benzyl 2-(Trimethylsilyl)ethynyl Selenide (9): Within a period of 10 min, *n*BuLi (1.35 mL, 2.16 mmol) was added dropwise through a rubber lid by using a syringe to a solution of trimethylsilylacetylene (TMSA; 0.21 g, 2.16 mmol) in dry THF (200 mL), cooled to –25 °C. Then it was stirred at –40 °C for 2 h. Compound **3** (0.61 g), dissolved in dry THF (100 mL), was added dropwise by using a cooled dropping funnel at –35 °C over a period of 1.5 h and then stirred for an additional 1 h. The pale-yellow reaction mixture was warmed to room temperature and mixed with a saturated NH_4Cl solution (60 mL), which resulted in the precipitation of a white solid. After adding light petroleum ether (80 mL), the layers were separated. The aqueous layer was further extracted three times with light petroleum ether (ca. 50 mL). The combined organic layers were washed with brine and dried with $MgSO_4$. The solvents were removed by rotary evaporation, and the resulting residue was purified by silica gel column chromatography using petroleum ether (b.p. 30–40 °C)/diethyl ether (10:1) as eluent to afford 259 mg (34%) of **9** as a colorless oil. MS (EI$^+$): *m*/*z* (%) = 362 (6.9) $[M]^+$, 347 (4.9) $[M - CH_3]^+$, 185 (64.2) $[M - SeC_5H_9Si]^+$, 169 (21.0) $[M - SeC_6H_{12}Si]^+$, 105 (100) $[SeC_2H_2]^+$. ^1H NMR (500 MHz, CD_2Cl_2): δ = 0.15 [s, 9 H, $Si(CH_3)_3$], 2.34 (s, $^2J_{Se,H}$ = 11.6 Hz, 3 H, $SeCH_3$), 4.15 (s, $^2J_{Se,H}$ = 15.8 Hz, 2 H, CH_2), 7.16–7.23 (m, 2 H, H_{arom}), 7.26 (dd, *J* = 7.1, 1.7 Hz, 1 H, H_{arom}), 7.46 (dd, *J* = 7.6, 1.1 Hz, 1 H, H_{arom}) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = –0.0 [3 C, *p*-$Si(CH_3)_3$], 8.2 (p-$SeCH_3$), 33.9 (s-CH_2), 86.8 (q-SeCC), 109.8 (q-SiCC), 126.6 (t-C_{arom}), 128.7 (t-C_{arom}), 130.4 (t-C_{arom}), 131.8 (t-C_{arom}), 133.3 (q-$C_{arom}SeCH_3$), 138.8 (q-$C_{arom}CH_2$) ppm. ^{77}Se NMR (95 MHz, CD_2Cl_2): δ = 157.2 ($SeCH_3$), 260.7 (SeC≡CTMS) ppm.

1,6-Bis[2′-(methylselenyl)phenyl]-2,5-diselena-3-hexyne (11): A yield of 82 mg (14%) of **11**, as thin white needles, was obtained as a secondary product of the synthesis of compound **9**. MS (EI): *m*/*z* (%) = 550.9 (0.9) $[M]^+$, 534.9 (11.2) $[M - CH_3]^+$, 366.9 (14.9) $[C_{10}H_9Se_3]^+$, 265.0 (73.6) $[C_8H_9Se_2]^+$, 249.9 (4.3) $[C_7H_6Se_2]^+$, 185.0 (91) $[C_8H_9Se]^+$, 105.0 (100) $[C_2HSe]^+$, 91.1 (38.9) $[C_7H_7]^+$. ^1H NMR (500 MHz, CD_2Cl_2): δ = 2.34 (s, $^2J_{Se,H}$ = 11.6 Hz, 3 H, $SeCH_3$), 4.10 (s, $^2J_{Se,H}$ = 15.6 Hz, 2 H, CH_2), 7.12 (dd, *J* = 7.5, 1.8 Hz, 1 H, H_{arom}), 7.16 (ddd, *J* = 7.5, 7.4, 1.3 Hz, 1 H, H_{arom}), 7.19 (ddd, *J* = 7.6, 7.4, 1.8 Hz, 1 H, H_{arom}), 7.45 (dd, *J* = 7.6, 1.3 Hz, 1 H, H_{arom}) ppm. ^{13}C NMR (125MHz, CD_2Cl_2): δ = 8.3 (p-$SeCH_3$), 35.0 (s-CH_2), 84.6 (q-C≡C), 126.7 (t-C_{arom}), 128.7 (t-C_{arom}), 130.5 (t-C_{arom}), 131.7 (t-C_{arom}), 133.3 (q-$C_{arom}SeCH_3$), 138.8 (q-$C_{arom}CH_2$) ppm. ^{77}Se NMR (95 MHz, CD_2Cl_2): δ = 159.8 ($SeCH_3$), 273.2 (SeC≡C) ppm. IR (film): $\tilde{\nu}$ = 3054 (w), 3003 (w), 2925 (m), 1688 (w), 1667 (w), 1584 (w), 1463 (m), 1439 (m), 1424 (m), 1268 (w), 1179 (w), 1055 (w), 1030 (m) cm^{-1}. HRMS (positive EI): calcd. for $^{12}C_{18}{}^1H_{18}{}^{78}Se^{80}Se^{82}Se$ $[M]^+$ 551.8077; found 551.8095 (+0.8 mmu).

Ethynyl 2-(Methylselenyl)benzyl Selenide (2): A 0.1 N NaOH solution was added dropwise to a solution of **9** (0.18 g, 0.5 mmol) in methanol (50 mL) and THF (10 mL) over a period of 5 min. The reaction mixture was stirred at room temperature for 2 h. Then the mixture was poured into ice/water (100 mL), and diethyl ether (100 mL) was added. The layers were separated, and the aqueous layer was then extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with NH_4Cl solution and brine and dried with $MgSO_4$. After rotary evaporation, the raw product was purified by silica gel column chromatography, eluting with light petroleum ether/diethyl ether (20:1) to afford 109 mg (76%) of pure **2** as a colorless oil. MS (EI): *m*/*z* (%) = 290 (4.9) $[M]^+$, 185 (45.5) $[M - SeC_2H]^+$, 169 (22.4) $[M - SeC_3H_4]^+$, 105 (100) $[SeC_2H_2]^+$. ^1H NMR (500 MHz, CD_2Cl_2): δ = 2.35 (s, $^2J_{Se,H}$ = 11.6 Hz, 3 H, $SeCH_3$), 2.93 (s, C≡CH), 4.19 (s, $^2J_{Se,H}$ = 14.9 Hz, 2 H, CH_2), 7.19 (td, *J* = 7.4, 1.4 Hz, 1 H, H_{arom}), 7.22 (td, *J* = 7.4, 1.8 Hz, 1 H, H_{arom}), 7.29 (dd, *J* = 7.1, 1.8 Hz, 1 H, H_{arom}) 7.47 (dd, *J* = 7.4, 1.4 Hz, 1 H, H_{arom}) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 8.3 (p-$SeCH_3$), 33.6 ($^1J_{Se,C}$ = 51.6 Hz, s-CH_2), 66.2 (t-CH), 90.2 (q-SeCCH), 126.8 (t-C_{arom}), 128.8 (t-C_{arom}), 130.2 (t-C_{arom}), 131.9 (t-C_{arom}), 133.4 (q-$C_{ar}SeCH_3$), 138.7 (q-$C_{arom}CH_2$) ppm. ^{77}Se NMR (95 MHz, CD_2Cl_2): δ = 157.5 ($^4J_{Se,Se}$ = 40.9 Hz, $SeCH_3$), 238.6 ($^4J_{Se,Se}$ = 40.9 Hz, SeC≡CH) ppm. IR (film): $\tilde{\nu}$ = 3277 (s), 3161

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(w), 2926 (w), 2615 (w), 2028 (w), 1912 (m), 1463 (m), 1440 (m), 1423 (m), 1269 (m), 1208 (m), 1184 (s), 1096 (m), 1054 (m), 1031 (s), 909 (m), 840 (m), 812 (m), 755 (vs) cm^{-1}. HRMS (positive EI): calcd. for $^{12}C_{10}{}^{1}H_{10}{}^{78}Se^{82}Se$ $[M]^+$ 289.9113; found 289.9126 (+0.3 mmu).

Benzyl Ethynyl Selenide (17): Benzyl ethynyl selenide was synthesized from benzyl selenocyanate (**18**) according to a procedure similar to that used for the synthesis of **2** from **3**. The intermediate benzyl 2-(trimethylsilyl)ethynyl selenide was synthesized from **18** before being transformed into **17**. To synthesize benzyl 2-(trimethylsilyl)ethynyl selenide, a solution of *n*BuLi in *n*-hexane (1.6 M solution) was added slowly to a solution of TMSA (1.0 g, 10.5 mmol) in dry THF (250 mL) at –25 °C in such a way that the temperature did not exceed –25 °C. After complete addition of *n*BuLi, the pale-yellow solution was stirred at –25 °C for 2 h. A solution of **18** (2.0 g, 10 mmol) in dry THF (100 mL) was slowly added to the reaction flask without allowing the temperature to exceed –20 °C. After the addition had been completed, the reaction mixture was stirred at a temperature below –10 °C for 2 h. At the end of this time, a saturated aqueous solution of NH_4Cl (ca. 75 mL) was added to the reaction mixture. The organic phase was extracted with light petroleum ether (3 × 125 mL), washed with water and brine, and then dried with $MgSO_4$. After removal of the solvent by rotary evaporation, the raw product was purified by column chromatography on deactivated silica gel using light petroleum ether/dichloromethane (2:1) to afford 1.50 g (5.6 mmol, 56% yield) of benzyl 2-(trimethylsilyl)ethynyl selenide as a pale-yellow oil. MS: (EI$^+$): *m*/*z* (%) = 268 (2) $[M]^+$, 253 (1) $[M - CH_3]^+$, 194 (1) $[M - C_3H_9Si]^+$, 171 (2) $[C_7H_7Se]^+$, 162 (4) $[C_4H_6SeSi]^+$, 147 (2) $[C_3H_3SeSi]^+$, 91 (100) $[C_7H_7]^+$, 73 (54.2) $[C_3H_9Si]^+$, 65 (14.5) $[C_5H_5]^+$. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.17 [s, 9 H, Si-$(CH_3)_3$], 4.02 (s, $^2J_{Se,H}$ = 15.7 Hz, 2 H, CH_2Se), 7.28 (tt, J = 8.4, 1.2 Hz, 1 H, H_{arom}), 7.31–7.35 (m, 4 H, H_{arom}) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = –0.0 [$^1J_{Si,C}$ = 52.9 Hz, p-Si$(CH_3)_3$], 33.2 ($^1J_{Se,C}$ = 56.3 Hz, p-CH_2), 86.8 (q-SeC), 109.8 (q-CSi), 127.9 (t-C_{arom}), 128.8 (2 C, t-C_{arom}), 129.3 (2 C, t-C_{arom}), 138.3 (q-$C_{arom}CH_2$) ppm. ^{77}Se NMR (95 MHz, CD_2Cl_2): δ = 269.3 ppm. IR (film): $\tilde{\nu}$ = 3063 (w), 3029 (m), 2958 (s), 2897 (m), 2088 (vs), 1495 (s), 1454 (m), 1262 (m), 1249 (vs), 1186 (m), 1067 (m), 862 (br. s), 760 (vs) cm^{-1}. HRMS (positive EI): calcd. for $^{12}C_{12}{}^{1}H_{16}{}^{28}Si^{80}Se$ $[M]^+$ 268.0187; found 268.0166 (–2.0 mmu). A solution of 0.1 N NaOH (5.6 mL) was added dropwise to a solution of benzyl 2-(trimethylsilyl)ethynyl selenide (1.5 g, 5.6 mmol) in methanol (40 mL) and THF (5 mL) over a period of 15 min. After stirring at room temp. for 2 h, the reaction mixture was poured into ice/water (100 mL) and extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with a saturated NH_4Cl solution and brine and dried with $MgSO_4$. After rotary evaporation, the raw product was further purified by using silica gel flash chromatography, eluting with *n*-hexane, to afford 0.58 g (2.9 mmol, 53% yield) of compound **17** as a yellow oil. MS (EI$^+$): *m*/*z* (%) = 196 (5) $[M]^+$, 169 (1) $[C_7H_7Se]^+$, 105 (5.4) $[C_2HSe]^+$, 91 (100) $[C_7H_7]^+$, 65 (14.5) $[C_5H_5]^+$. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 2.93 (s, 1 H, CH), 4.05 (s, $^2J_{Se,H}$ = 14.8 Hz, 2 H, CH_2Se), 7.27 (tt, J = 6.5, 1.9 Hz, 1 H, H_{arom}), 7.31–7.36 (m, 4 H, H_{arom}) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 32.7 ($^1J_{Se,C}$ = 52.4 Hz, 2 C, s-CH_2), 66.0 (2 C, t-CH), 90.1 ($^1J_{Se,C}$ = 38.4 Hz, 2 C, q-SeC), 127.9 (t-C_{arom}), 128.9 (2 C, t-C_{arom}), 129.2 (2 C, t-C_{arom}), 138.1 (q-$C_{arom}CH_2$) ppm. ^{77}Se NMR (95 MHz, CD_2Cl_2): δ = 245.4 ppm. IR (film): $\tilde{\nu}$ = 3279 (vs), 3084 (w), 3028 (m), 2936 (w), 2029 (m), 1949 (w), 1877 (w), 1494 (vs), 1454 (s), 1418 (s), 1218 (m), 1188 (m), 1067 (m), 1029 (m), 759 (s), 696 (vs) cm^{-1}. HRMS (positive EI): calcd. for $^{12}C_9{}^{1}H_8{}^{80}Se$ $[M]^+$ 195.9791; found 195.9809 (+1.8 mmu).

Supporting Information (see footnote on the first page of this article): NMR spectra of the synthesized compounds (S1–S22) and absolute energies, Cartesian coordinates, as well as isotropic magnetic shieldings for the calculated conformers (S23–S28).

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[1] a) J. W. Steed, J. L. Atwood, *Supramolecular Chemistry: A Concise Introduction*, Wiley, Chichester, **2000**; b) H.-J. Schneider; A. K. Yatsimirsky, *Principles and Methods in Supramolecular Chemistry*, Wiley, Chichester, **2000**.

[2] a) J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, **1995**; b) F. Vögtle, *Supramolekulare Chemie*, Teubner, Stuttgart, **1992**; c) D. Philp, J. F. Stoddart, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1155–1196.

[3] a) D. T. Bong, T. D. Clark, J. R. Granja, M. R. Ghadiri, *Angew. Chem. Int. Ed.* **2001**, *40*, 988–1011; b) J. D. Hartgerink, T. D. Clark, M. R. Ghadiri, *Chem. Eur. J.* **1998**, *4*, 1367–1372.

[4] a) C. H. Gorbitz, *Chem. Eur. J.* **2001**, *7*, 5153–5159; b) C. H. Gorbitz, E. Gundersen, *Acta Crystallogr., Sect. C* **1996**, *52*, 1764–1767.

[5] W. Saenger in *Inclusion Compounds* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol), Academic Press, London, **1984**, vol. 2, pp. 231–259.

[6] a) D. Venkataraman, S. Lee, J. Zhang, J. S. Moore, *Nature* **1994**, *371*, 591–593; b) O. Henze, D. Lentz, A. D. Schlüter, *Chem. Eur. J.* **2000**, *6*, 2362–2367; c) S. Höger, D. L. Morrison, V. Enkelmann, *J. Am. Chem. Soc.* **2002**, *124*, 6734–6736.

[7] a) J. M. Williams, J. R. Ferraro, R. J. Thorn, *Organic superconductors (including fullerenes) – Synthesis structure, properties, and theory*, Prentice-Hall, Englewood Cliffs, NJ, **1992**; b) G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, **1989**.

[8] a) D. B. Werz, T. H. Staeb, C. Benisch, B. J. Rausch, F. Rominger, R. Gleiter, *Org. Lett.* **2002**, *4*, 339–342; b) D. B. Werz, R. Gleiter, F. Rominger, *J. Am. Chem. Soc.* **2002**, *124*, 10638–10639; c) R. Gleiter, D. B. Werz, B. J. Rausch, *Chem. Eur. J.* **2003**, *9*, 2676–2683; d) D. B. Werz, R. Gleiter, F. Rominger, *J. Org. Chem.* **2004**, *69*, 2945–2952; e) R. Gleiter, D. B. Werz, *Chem. Lett.* **2005**, *34*, 126–131.

[9] a) D. B. Werz, R. Gleiter, F. Rominger, *J. Org. Chem.* **2002**, *67*, 4290–4297; b) D. B. Werz, R. Gleiter, *J. Org. Chem.* **2003**, *68*, 9400–9405; c) D. B. Werz, B. J. Rausch, R. Gleiter, *Tetrahedron Lett.* **2002**, *43*, 5767–5769; d) D. B. Werz, R. Gleiter, F. Rominger, *Organometallics* **2003**, *22*, 843–849; e) D. B. Werz, F. R. Fischer, S. C. Kornmayer, F. Rominger, R. Gleiter, *J. Org. Chem.* **2008**, *73*, 8021–8029.

[10] a) J. H. Schulte, D. B. Werz, F. Rominger, R. Gleiter, *Org. Biomol. Chem.* **2003**, *1*, 2788–2794.

[11] a) R. E. Rosenfield Jr, R. Parthasarathy, J. D. Dunitz, *J. Am. Chem. Soc.* **1977**, *99*, 4860–4862; b) N. Ramasubbu, R. Parthasarathy, *Phosphorus Sulfur Relat. Elem.* **1987**, *31*, 221–229; c) J. P. Glusker, *Top. Curr. Chem.* **1998**, *198*, 1–56.

[12] a) C. Bleiholder, D. B. Werz, H. Köppel, R. Gleiter, *J. Am. Chem. Soc.* **2006**, *128*, 2666–2674; b) C. Bleiholder, R. Gleiter, D. B. Werz, H. Köppel, *Inorg. Chem.* **2007**, *46*, 2249–2260.

[13] a) W. Nakanishi, Y. Ikeda, H. Iwamura, *Org. Magn. Reson.* **1982**, *20*, 117–122; b) N. P. Luthra, J. D. Odom, *Nuclear Magnetic Resonance and Electron Spin Resonance Studies of Organic Selenium and Tellurium Compounds* (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1986**, vol. 1, pp. 189–241.

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[14] a) T. Wirth, *Angew. Chem.* **2000**, *112*, 3891–3900; *Angew. Chem. Int. Ed.* **2000**, *39*, 3740–3749; b) M. Tiecco, *Top. Curr. Chem.* **2000**, *208*, 7–54; c) M. Iwaoka, S. Tomoda, *Top. Curr. Chem.* **2000**, *208*, 55–80.
[15] a) M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli, M. Montanucci, *J. Org. Chem.* **1983**, *48*, 4289–4296; b) D. J. Gulliver, E. G. Hope, W. Levason, S. G. Murray, D. M. Potter, G. L. Marshall, *J. Chem. Soc. Perkin Trans. 2* **1984**, 429–434; c) M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli, M. Montanucci, *Synth. Commun.* **1983**, *13*, 617–620.
[16] P. J. Kociensky, *Protecting Groups*, Thieme, Stuttgart, **1994**.
[17] Y. Tamura, M. Adachi, T. Kawasaki, Y. Kita, *Tetrahedron Lett.* **1979**, *20*, 2251–2252.
[18] a) L. B. Agenas, *Acta Chem. Scand.* **1963**, *17*, 268–270; b) P. T. Meinke, G. A. Krafft, A. Guram, *J. Org. Chem.* **1988**, *53*, 3632–3634.
[19] C. Eaborn, R. Eastmond, D. R. M. Walton, *J. Chem. Soc. B* **1971**, 127–130.
[20] F. H. Allen, *Acta Crystallogr., Sect. B* **2002**, *58*, 380–388.
[21] A. J. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451.
[22] a) T. Steiner, *Angew. Chem. Int. Ed.* **2002**, *41*, 48–76; b) G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bond: Application to Structural Chemistry and Biology*, Oxford University Press, Oxford, **1999**.
[23] M. Iwaoka, S. Tomoda, *J. Am. Chem. Soc.* **1994**, *116*, 4463–4464.
[24] a) M. Iwaoka, H. Komatsu, T. Katsuda, S. Tomoda, *J. Am. Chem. Soc.* **2002**, *124*, 1902–1909; b) M. Iwaoka, H. Komatsu, T. Katsuda, S. Tomoda, *J. Am. Chem. Soc.* **2004**, *126*, 5309–5317; c) M. Iwaoka, T. Katsuda, H. Komatsu, S. Tomoda, *J. Org. Chem.* **2005**, *70*, 321–327.
[25] a) W. Nakanishi, S. Hayashi, A. Sakaue, G. Ono, Y. Kawada, *J. Am. Chem. Soc.* **1998**, *120*, 3635–3640; b) W. Nakanishi, S. Hayashi, T. Uehara, *J. Phys. Chem. A* **1999**, *103*, 9906–9912; c) W. Nakanishi, S. Hayashi, S. Toyota, *Chem. Commun.* **1996**, 371–372.
[26] M. Tiecco, L. Testaferri, C. Santi, C. Tomassini, S. Santoro, F. Marini, L. Bagnoli, A. Temperini, F. Costantino, *Eur. J. Org. Chem.* **2006**, 4867–4873.
[27] a) H. Duddeck, *Annu. Rep. NMR Spectrosc.* **2004**, *52*, 105–166; b) H. Duddeck, *Prog. Nucl. Magn. Reson. Spectrosc.* **1995**, *27*, 1–323.
[28] M. H. Levitt, *Spin Dynamics: basics of nuclear magnetic resonance*, Wiley, Chichester, **2001**.
[29] a) W. P. Aue, E. Bartholdi, R. R. Ernst, *J. Chem. Phys.* **1976**, *64*, 2229–2246; b) K. Nagayama, A. Kumar, K. Wuethrich, R. R. Ernst, *J. Magn. Reson.* **1980**, *40*, 321–334.
[30] R. S. Laitinen, T. A. Pakkanen, *Inorg. Chem.* **1987**, *26*, 2598–2603.
[31] a) W. Nakanishi, S. Hayashi, H. Yamaguchi, *Chem. Lett.* **1996**, 947–948; b) W. Nakanishi, S. Hayashi, *Chem. Eur. J.* **2008**, *14*, 5645–5655.
[32] a) W. Kohn, L. J. Sham, *Phys. Rev. A: At. Mol. Opt. Phys.* **1965**, *140*, 1133–1138; b) R. G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, **1989**; c) W. Koch, M. C. Holthausen, A *Chemists Guide to Density Functional Theory*, Wiley-VCH, Weinheim, **2000**.
[33] a) A. D. Becke, *J. Chem. Phys.* **1992**, *96*, 2155–2160; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; c) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372–1377.
[34] a) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785–789; b) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623–11627.
[35] a) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650–654; b) A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639–5648; c) L. A. Curtiss, M. P. McGrath, J.-P. Blaudeau, N. E. Davis, R. C. Binning Jr., L. Radom, *J. Chem. Phys.* **1995**, *103*, 6104–6113.
[36] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burnat, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision C.01*, Gaussian, Inc., Wallingford, CT, **2004**.
[37] H. L. Schmider, A. D. Becke, *J. Chem. Phys.* **1998**, *108*, 9624–9631.
[38] C. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618–622.
[39] F. London, *J. Phys. Radium* **1937**, *8*, 397–409.
[40] a) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868; b) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 1396.
[41] A. Schaefer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829–5835.
[42] G. M. Sheldrick, *SADABS 2008/1*, Bruker Analytical X-ray Division, Madison, WI, **2008**.
[43] SHELXTL 2008/1: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

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