Alkenyl Selenols and Selenocyanates: Synthesis, Spectroscopic Characterization by Photoelectron Spectroscopy, and Quantum Chemical Study

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Abstract: Vinyl, allyl, and homoallyl selenols were easily prepared by a chemoselective reduction of the corresponding selenocyanates with aluminum hydrides. Two stable vinyl and five stable allyl conformers of both series were predicted on the potential-energy surface. The interaction of SeH or SeCN groups with the vinyl group has been investigated with UV photoelectron spectroscopy and quantum chemical calculations, using the MP2/cc-pVTZ and B3LYP/cc-pVTZ levels. In the vinyl derivatives, a surprisingly strong direct conjugation of the selenium lone electron pair and the C=C double bond was observed. On the other hand, in allyl position the selenium lone pair is independent on the C=C double bond, and the hyperconjugation between the Se−C bond and the double bond is the ruling effect. Thus is clarified the type and extent of the interaction between the SeH or SeCN group and the unsaturated moiety.

Keywords: ab initio calculations · photoelectron spectroscopy · selenium · selenocyanates · selenols

Introduction

It is generally accepted, that the lone electron pair of the heavier Group 15 elements interacts only weakly with neighboring π systems, since the lone pair of the heteroatom is mainly of "s" type and is situated in the nodal surface of the π bond.[1] On the other hand, these heteroatoms usually interact strongly with π systems in the allylic position through the σ_{C-E} or σ_{C-E*} orbital. This so-called β effect has significant impact on spectroscopic characteristics[2] and reaction rates.[3] The importance of this effect has been demonstrated in case of allylic phosphines and arsines.[4,5] In our earlier work we investigated several allylic phosphines and arsines by photoelectron spectroscopy and high-level quantum chemical calculations and we demonstrated that the most stable structure of these compounds is when the C−E (E = P, As) bond is out of the plane of the allyl system.[5] This conformation is inevitably stabilized by the hyperconjugation between the π system and the C−E σ^* orbital. From the difference between the planar and nonplanar conformation the stabilization energy could be estimated to 2–3 kcal mol^{-1}. The splitting of the appropriate photoelectron bands indicated that the interaction increased towards the heavier heteroatoms.

Considering the Group 16 elements, spectroscopic evidence suggests the importance of hyperconjugation between the unsaturated group and the sulfur atom in some allyl sulfide derivatives.[6] The photoelectron spectra of ethenethiol and 1-propene-1-thiol indicates, however, a direct interaction between the π_{C-C} and the lone electron pair of the sulfur atom.[7] Such an interaction can be excluded in case of the respective oxygen derivatives, because of the huge electronegativity of oxygen. The electronegativity of selenium is, however, close to that of sulfur. Therefore similar structural and spectroscopic characteristics are expected in the selenium and sulfur derivatives.

The interaction of the −SeCN group with an unsaturated fragment opens some new questions. Microwave spectroscopic studies have shown that alkyl cyanates, thiocyanates, and selenocyanates have a bent frame.[8] These compounds are very rigid; the barrier to linearity is high[9] and the observed C-X-C (X = O, S, Se) angles are 113°, 99° and 96°, respectively.[8a,c,e] Alkyl isocyanates, isothiocyanates, and isoselenocyanates, on the other hand, are much more flexible than their isomeric counterparts. The C-N-C bond angle at the equilibrium geometry is 140.0° for CH_3NCO, 150.9° for CH_3NCS, and 161.7° for CH_3NCSe, and the potential barriers to linearity are 928, 193, and 25 cm^{-1}, respectively.[10] The barrier is so small for the isoselenocyanate that all vi-

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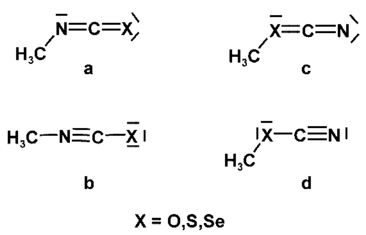
brational levels lie above this, hence the molecule is effectively linear. In this and several other related compounds low-energy large-frequency vibrations often complicate the structural investigations. Therefore the most careful experimental and theoretical analysis is required to avoid the misinterpretation.[11] The close relationship between the geometric and electronic structure of these molecules is explained in the diagram below.



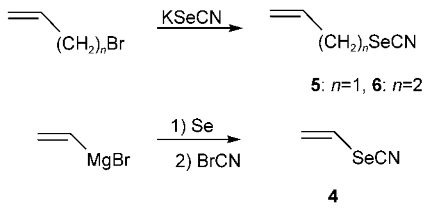
While the structure of molecules CH_3NCX changes gradually from **a** to **b**, the structure of CH_3XCN changes from **c** to **d** in the series X = O, S and Se.

The aim of this work was to study the structural and electronic properties of the simplest vinyl, allyl, and homoallyl selenols **1**–**3** and selenocyanates **4**–**6** and to clarify the type and extent of the interaction between the SeH or SeCN group and the unsaturated moiety. For the selenocyanates another question is the possible conjugation of the two unsaturated fragments. The recent synthesis of compounds **1**–**3**[12,13] allows us to investigate these questions in experimental and theoretical approaches. To the best of our knowledge, we here report the first study by photoelectron spectroscopy devoted to aliphatic selenols. Since even the spectrum of the simplest alkyl derivative, the methaneselenol, has never been described, this spectrum is added to this work to use it as a reference.

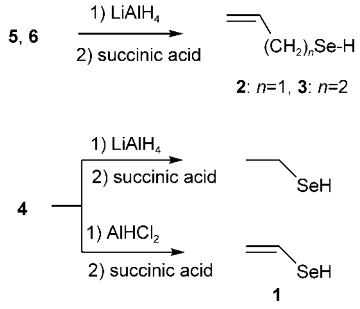
$H_2C{=}CH{-}SeH$ 1	$H_2C{=}CH{-}CH_2{-}SeH$ 2	$H_2C{=}CH{-}CH_2{-}CH_2{-}SeH$ 3
$H_2C{=}CH{-}SeCN$ 4	$H_2C{=}CH{-}CH_2{-}SeCN$ 5	$H_2C{=}CH{-}CH_2{-}CH_2{-}SeCN$ 6

Results and Discussion

Synthesis of compounds 1–6: Selenocyanates **5** and **6** were prepared by reaction of the corresponding bromide derivative with potassium selenocyanate.[12] However, this approach cannot be extended to vinyl halides. The vinyl ester of selenocyanic acid was prepared by reaction of the vinyl selenolate with cyanogen bromide in a 71% yield (Scheme 1). Compounds **2** and **3** were prepared by reaction of lithium aluminum hydride with compounds **5** and **6**, respectively, followed by acidification of the formed selenolate with succinic acid.[12] As already reported, such an approach applied to α,β-unsaturated selenocyanates only leads to the formation of the corresponding saturated selenols.[12] Although the etheneselenol (**1**) can be prepared by the reaction of divinyldiselenide with tributyltin hydride,[13] we were looking to extend our approach starting from selenocyanates to the preparation of α,β-unsaturated selenols. We found that the use of dichloroalane as the reducing agent allows the formation of etheneselenol (**1**) in a 66% yield after acidification with succinic acid (Scheme 2). No traces of ethaneselenol were observed in these experimental conditions. The chemoselectivity of this reduction is consistent with other reductions performed for the preparation of α,β-unsaturated phosphines,[14] and this result opens the way to the preparation of many other α,β-unsaturated selenols.



Scheme 1.

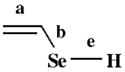
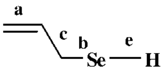
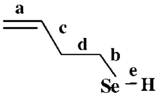
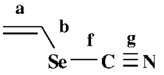
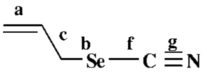
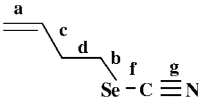


Scheme 2.

Structures: The calculated structural parameters and energy data of the investigated compounds are compiled in Tables 1 and 2. Two stable conformations of vinyl derivatives were found on the potential-energy surface: the planar *syn* and *anti* forms (Figures 1 and 2). The energy difference between them is only a few tenths of $kcal\,mol^{-1}$ for selenol and somewhat larger for selenocyanate (0.34–1.05 $kcal\,mol^{-1}$, depending on the computational method, see Table 2). Recent G3(MP2) data[15] for the energy difference between the two etheneselenol rotamers ($\Delta E = 0.35\ kcal\,mol^{-1}$) supports the reliability of our results. No significant difference in the geometrical parameters or in the calculated ionization energies could be found. The activation barrier between the two selenol conformers is 1.7 $kcal\,mol^{-1}$ and between the selenocyanates **4a** and **4b** is 2.3 $kcal\,mol^{-1}$; this indicates that the rotation of the SeH or SeCN group is free only at high temperature.

The C=C and the Se–C bond lengths of **1** are 1.334 and 1.887 Å, respectively, the former is slightly longer, the latter is considerably shorter than those in ethene (1.332 Å) and methaneselenol (1.951 Å). The same bond lengths in the

Table 1. Calculated bond lengths of selenols and selenocyanates [in Å].[a]

Molecule	Conformation	Geometrical Parameter a	b	c	d	e	f	g
	**1a**	1.334 (1.325)	1.887 (1.911)			1.453 (1.473)		
	1b	1.334 (1.325)	1.892 (1.917)			1.450 (1.469)		
	**2a**	1.335 (1.328)	1.961 (2.004)	1.489 (1.487)		1.453 (1.473)		
	2b	1.335 (1.328)	1.960 (2.001)	1.487 (1.487)		1.453 (1.472)		
	2c	1.336 (1.328)	1.957 (1.997)	1.486 (1.486)		1.452 (1.472)		
	2d	1.333 (1.325)	1.951 (1.986)	1.494 (1.495)		1.452 (1.471)		
	2e	1.333 (1.325)	1.944 (1.978)	1.497 (1.499)		1.453 (1.472)		
	**3a**	1.335 (1.327)	1.947 (1.982)	1.497 (1.502)	1.525 (1.530)	1.453 (1.473)		
	3b	1.335 (1.327)	1.947 (1.983)	1.494 (1.499)	1.528 (1.531)	1.453 (1.472)		
	**4a**	1.332 (1.323)	1.900 (1.927)				1.828 (1.847)	1.176 (1.155)
	4b	1.331 (1.321)	1.898 (1.925)				1.822 (1.843)	1.177 (1.155)
	**5a**	1.335 (1.328)	1.967 (2.016)	1.488 (1.486)			1.827 (1.845)	1.177 (1.156)
	5b	1.335 (1.328)	1.967 (2.014)	1.486 (1.484)			1.824 (1.843)	1.177 (1.156)
	5c	1.336 (1.328)	1.971 (2.015)	1.482 (1.482)			1.822 (1.843)	1.177 (1.156)
	5d	1.333 (1.325)	1.955 (1.994)	1.493 (1.493)			1.825 (1.844)	1.177 (1.156)
	5e	1.332 (1.324)	1.947 (1.985)	1.496 (1.497)			1.826 (1.845)	1.177 (1.156)
	**6a**	1.348 (1.327)	1.970 (1.991)	1.507 (1.503)	1.531 (1.527)		1.844 (1.845)	1.191 (1.156)

[a] MP2/cc-pVTZ calculations. Data of B3LYP/cc-pVTZ level are in brackets.

Table 2. Calculated total energies [a.u.] and relative energies [kcal mol^{-1}].

Molecule	Conformation	E_{tot}		E_{rel}	
		MP2/cc-pVTZ	B3LYP	MP2	B3LYP
H_2C=CHSeH	**1a**	−2478.50017	−2480.25239	0.00	0.00
	1b	−2478.49962	−2480.25214	0.34	0.05
H_2C=CHCH$_2$SeH	**2a**	−2517.72382	−2519.58231	1.00	0.82
	2b	−2517.72363	−2519.58218	1.12	0.88
	2c	−2517.72542	−2519.58363	0.00	0.00
	2d	−2517.72161	−2519.57886	2.39	2.82
	2e	−2517.72297	−2519.58010	1.53	2.15
H_2C=CHCH$_2$CH$_2$SeH	**3a**	−2556.94680	−2558.91002	0. 66	−0.27
	3b	−2556.94784	−2558.90959	0. 00	0.00
H_2C=CHSeCN	**4a**	−2570.57503	−2572.51426	0.00	0.00
	4b	−2570.57337	−2572.51370	1.05	0.27
H_2C=CHCH$_2$SeCN	**5a**	−2609.80027	−2611.84696	1.27	0.26
	5b	−2609.80058	−2611.84667	1.08	0.42
	5c	−2609.80230	−2611.84738	0.00	0.00
	5d	−2609.79755	−2611.84285	2.98	2.58
	5e	−2609.79883	−2611.84319	2.18	2.45
H_2C=CHCH$_2$CH$_2$SeCN	**6a**	−2648.61702	−2651.17474		

transition state of **1** during rotation are 1.332 and 1.911 Å, respectively. The calculated geometrical parameters of **4** are in good agreement with the microwave spectroscopical results of CH_3SeCN (C–Se: 1.954 Å, Se–C: 1.836 Å, C–N: 1.162 Å, C-Se-C: 96°) and ethene (C=C: 1.332).[8e] The pseudohalogeno group is linear and strongly bent at the selenium (the C-Se-C bond for both conformers is around 96° or 98° depending on the method). The only important difference from the two parent compounds can be observed again in the Se–(C=C) bond which has been reduced to 1.900 Å. The data indicates a strong interaction between the π system and the selenium lone pair. Also, it seems that the CN group is remarkably insensitive to the interactions with the rest of the molecule.

Five minima were found on the potential surface of both allyl derivatives **2** and **5** as shown in Figure 1, 2 and Table 2. The three lowest energy structures (refered to as **A** conformations) are when the selenium atom is out of the plane of the allylic unit (**2a–c** and **5a–c**). These structures differ only by the direction of the Se–H or Se–CN bond and their energy differences are very small. In the minima (**2d**,**e** and **5d**,**e**, named **B** conformations), the selenium atom is situated in the plane of the allyl group. Hyperconjugation can be realized only in the **A** type conformers, which are indeed the most stable compounds. Although the stabilization energy relative to **B** is less than 3 kcal mol^{-1}, this is enough energy to keep the majority of the molecules in one of the **A** conformations. It is worth noting that this energy difference is close to the values obtained for β-substituted ethyl radicals,[16] and in allylphosphines and -arsines.[5]

In accordance with the small energy separation, the bond length of the **A** and **B** type structures varies only slightly, but systematically. The double bond and the C–Se bond is somewhat longer, the C–C single bond is shorter in **A** than in **B**. The geometry variation of the SeCN group is negligible. Comparing to the isolated subunits propene, methaneselenol (C=C 1.334 Å, C–C 1.505 Å, C–Se 1.951 Å) and meth-

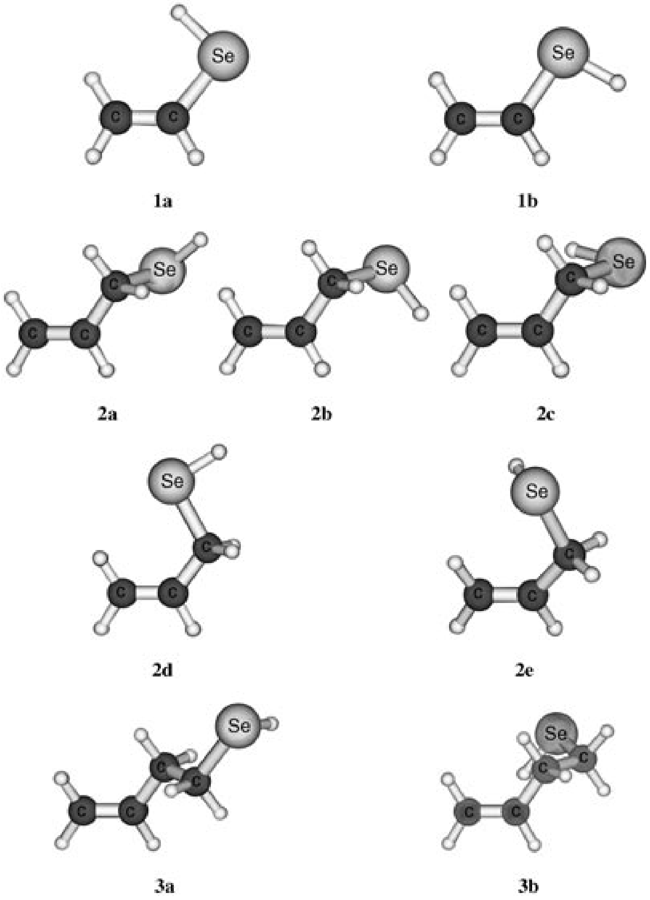


Figure 1. Stable alkenyl selenol conformers.

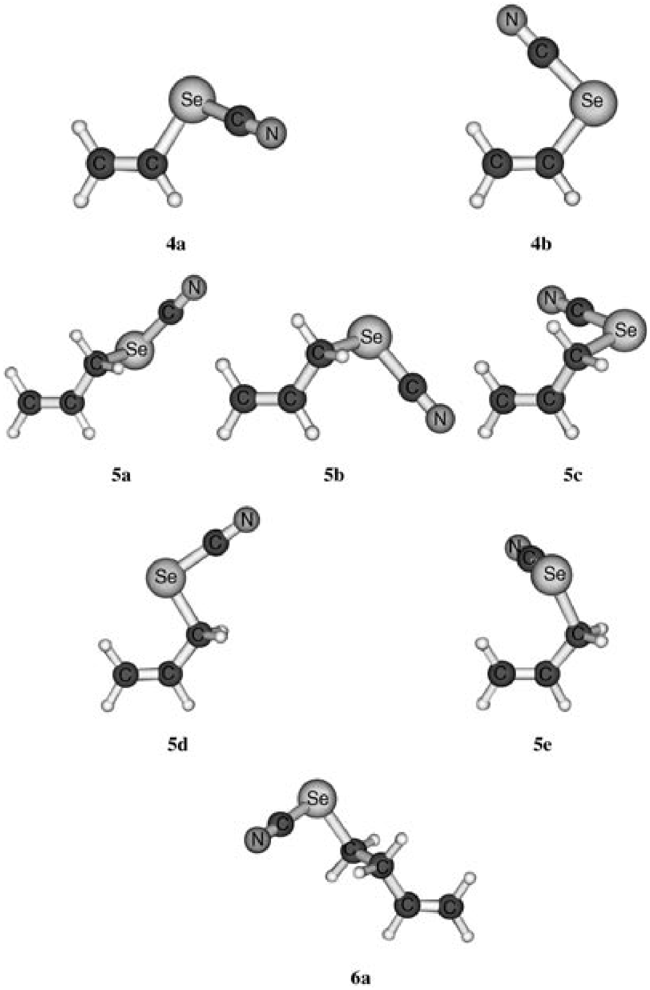


Figure 2. Stable alkenyl selenocyanate conformers.

aneselenocyanate (C–Se: 1.942 Å, Se–C: 1.826 Å, C≡N: 1.177 Å), the direction of the slight changes is the same: especially the enhanced C–Se bond is conspicuous. Such behavior can be expected if hyperconjugation occurs with the C–Se σ orbital. Again, the geometrical parameters of the SeCN group (bond lengths and the C-Se-C angle) are unchanged.

Recent G2(MP2) calculations and microwave spectroscopical measurements suggested that only three rotamers out of the 14 different 3-buteneselenol conformers play important role in the behavior of this compound.[17] The lowest energy rotamer has an internal hydrogen bond between the hydrogen atom of the selenol group and the π electrons of the double bond (Figure 1, **3b**). As we want to investigate and compare the pure interaction between the selenium and the C=C bond, in addition to the lowest energy structure we studied a slightly higher energy (0.1 kcal mol^{-1}) conformer (Figure 1, **3a**) in which, according to the calculation, the main bond lengths are almost the same. Although similar microwave study of the respective selenocyanates is still missing, we assumed the same tendencies and selected a related conformer for investigation (Figure 2, **6a**). In **3** and **6** it can be assumed that the interaction with the distant selenium is negligible and only the inductive (and some steric) effect of CH_2 groups is responsible for the geometrical and spectroscopic properties. Indeed, the C=C, C–C, and C–Se bond lengths are close to the "usual" values observable in the separated propene, methaneselenol, and methaneselenocyanate.

Photoelectron spectroscopy: The observed UV photoelectron spectra of the investigated compounds are reported in Figure 3. The position of the most important photoelectron bands and the calculated vertical ionization energies using the ROVGF method (for the most stable conformers) and the Koopmans' theorem (for all conformers) are collected in Table 3. The ROVGF results are in general in excellent agreement with the experimental data. The agreement with the MO energies is worse, but a good linear correlation with the PE bands suggests the validity and applicability of the Koopmans' theorem.

The ethene-, 2-propene-, and 3-buteneselenols **1**–**3** can be characterized by their three lowest ionization energy bands, which can be attributed to the lone electron pair of selenium, the π system, and the Se–C bond. Therefore the systematic study of these bands may also reflect the extent and character of the intramolecular interactions. The spectra of pseudohalogenides are somewhat more complicated. The electronic structure of the SeCN group can be explained in two ways. We can assume a single Se–C bond and a triple C≡N bond. In this case the appearance of two new bands

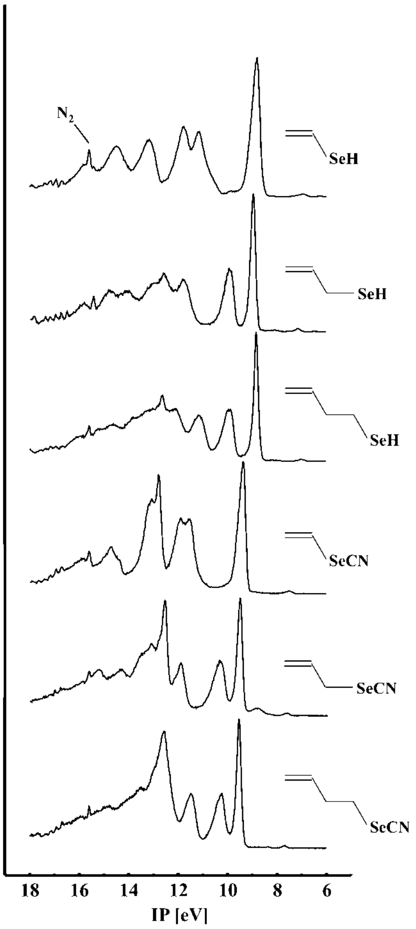


Figure 3. Photoelectron spectra of the investigated compounds.

(the C≡N π bonds) is expected in the low-energy region of the spectrum. Another interpretation is when the SeCN unit is considered as two perpendicular four-electron three-centre π systems, which suggests four new bands in the spectrum (the high-energy π_1 and $\pi_1\perp$ and the low-energy π_2 and $\pi_2\perp$). If the molecular skeleton is linear (e.g., in CH_3–NCSe), the perpendicular MO pairs are degenerate. In case of the strongly bent X–SeCN, theoretically the appearance of all the four π bands are expected. However, the selenium lone pair in the SeCN group is part of a π system and the σ(C–Se) orbital is also part of the perpendicular π system. As a summary, only two additional bands are expected in the small energy spectrum region.

Since several conformers with comparable energies are possible in some cases, first we should investigate whether the spectra can originate from a mixture of all conformers or only some of them dominate. No noticeable difference can be found between the orbital energies of the two stable conformers of **1** and **4**, therefore our discussion is reduced to the analysis of the slightly more stable conformer I. In the case of allyl derivatives **2** and **5**, the orbital energies of all **A** structures are close to each other. Also, the ionization energies of the **B** conformers are nearly the same. The two sets, however, exhibit some differences. There is no difference in the first ionization energy of selenol: it is almost the same in all the five conformers. Since the first band belongs to the lone electron pair of selenium, this finding suggests that the n_{Se} orbital does not interact with other molecular orbitals. While the **B** conformation strongly stabilizes the second π band and destabilizes the third C–Se band, the effect in the case of the **A** structures is just the opposite.

Table 3. Experimental and calculated[a] ionization energies [eV].

Molecule	IE_{exptl}			IE_{calcd}					assignment
		a		**b**	**c**		**d**	**e**	
$H_2C{=}CH{-}SeH$	8.80	8.72	*8.74*	8.70					$n_{Se}-\pi$
	11.23	11.93	*11.46*	11.92					$n_{Se}+\pi$
	11.73	12.23	*11.92*	12.06					σ(C–Se)
	13.24	13.83	*13.24*	14.10					σ
$H_2C{=}CH{-}CH_2{-}SeH$	8.95	9.15		9.13	9.14	*8.89*	9.14	9.20	n_{Se}
	9.96	10.05		10.00	10.04	*9.86*	10.27	10.20	π
	11.81	12.13		12.33	12.24	*11.88*	11.71	11.74	σ(C–Se)
	12.69	13.59		13.76	13.93	*13.20*	13.44	13.61	
$H_2C{=}CH{-}CH_2{-}CH_2{-}SeH$	9.11	8.85	*8.86*	9.04					n_{Se}
	9.91	10.14	*9.95*	10.11					π
	11.13	11.65	*11.25*	11.56					σ(C–Se)
	12.06	13.27	*12.59*	13.04					
$H_2C{=}CH{-}SeCN$	9.40	9.82	*9.30*	9.51					$\pi-\pi_2$
	11.58	11.94	*11.55*	12.33					$\pi+\pi_2$
	11.95	12.47	*11.88*	12.62					$\pi_2\perp$
	12.81	14.01	*13.05*	14.07					$\pi_1\perp$
	13.08	14.26	*13.23*	14.35					π_1
	14.71	15.03	*14.63*	14.94					σ
$H_2C{=}CH{-}CH_2{-}SeCN$	9.54	9.91		9.87	9.87	*9.48*	9.94	9.98	$\pi_2\perp$
	10.31	10.61		10.51	10.47	*10.14*	10.87	10.62	π
	11.93	12.59		12.61	12.50	*11.76*	12.14	12.13	π_2
	12.57	13.87		13.92	13.82	*12.60*	13.93	13.89	π_1
	12.9	14.06		14.17	14.04	*12.96*	14.01	13.91	$\pi_1\perp$
$H_2C{=}CH{-}CH_2{-}CH_2{-}SeCN$	9.54	9.86	*9.13*						$\pi_2\perp$
	10.16	10.47	*9.96*						π
	11.46	12.10	*11.19*						π_2
	12.56–12.97	13.65–13.84	*12.20–12.43*						$\pi_1\perp$, π_1

[a] Regular numbers indicate the results calculated with the Koopmans' theorem, numbers in italics indicate the OVGF results.

The latter is in good agreement with the experimental spectrum. The inspection of the calculated MO's reveals the difference. In the **B**-type structures, the second and third orbitals are separately localized on the C=C and the C–Se bonds, respectively, but in the **A** structures the two orbitals are mixed.

The comparison of the **A** and **B** structures of selenocyanates leads to the same conclusion. The first band, which originates now from one of the components of the π_2 orbital, is not sensitive to the rotation of the SeCN group. The **B** conformation stabilizes the second band, which belongs to the C=C bond, and destabilizes the third band, which belongs to the perpendicular π_2 orbital, while the **A** conformation only slightly stabilizes the second band and more strongly the third one.

Starting from the experimental PE spectra of methaneselenol and propene, a clear correlation of the respective bands can be seen (Figure 4). While in the spectrum of buteneselenol **3** the ionization energies are close to those of the parent compounds, the shape of the first three orbitals are almost unchanged (relative to the parent compounds). The band shifts can be explained with the difference of the inductive effect; in the case of the allyl derivative **2**, the first two bands shift only slightly, but the third band strongly stabilizes in good agreement with the assumed **A** structure and the consequence of the hyperconjugation.

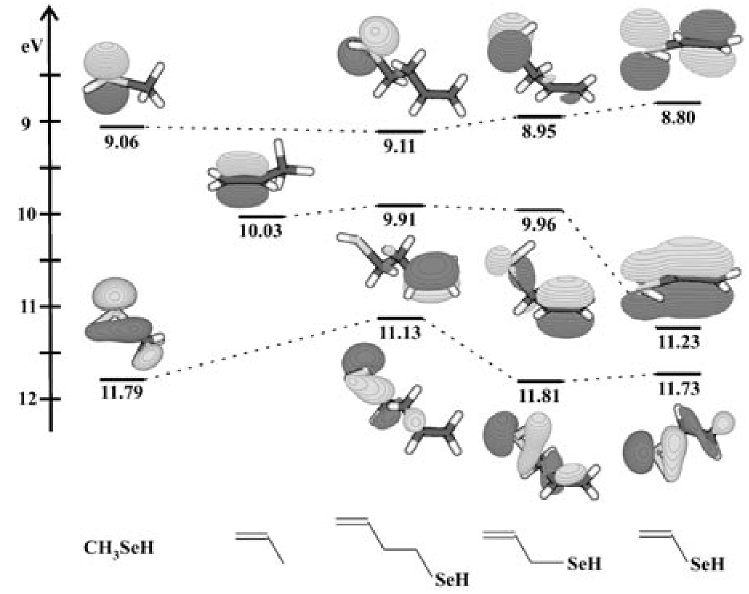


Figure 4. Correlation between the observed photoelectron bands in alkenyl selenols.

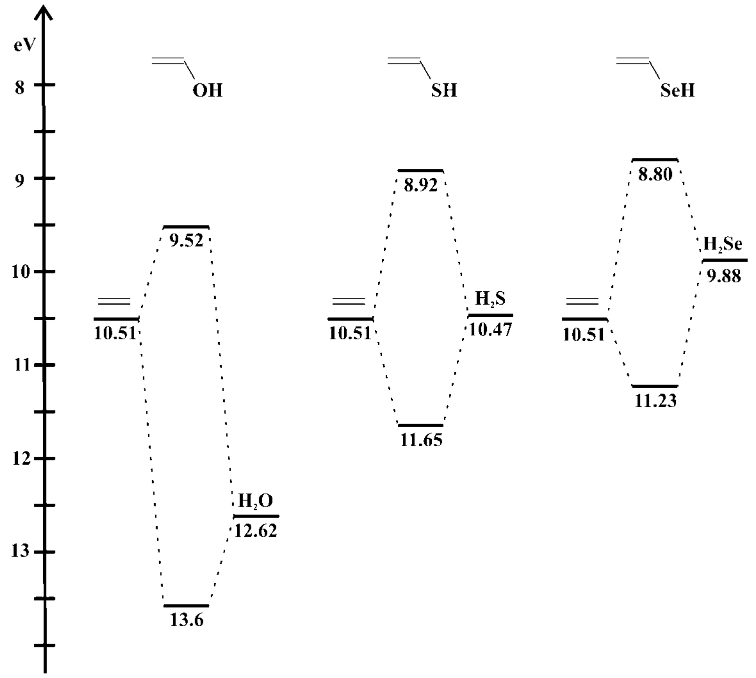


Figure 5. Interaction between the lone pair and the double bond in vinyl–XH derivatives (X = O, S, Se). The data are given from the observed photoelectron spectra.

Different effects can be observed studying the PE bands of etheneselenol, for which a huge splitting of the first two bands can be seen. The interaction of the C=C double bond and the lone electron pair of same symmetry in the vinyl derivative can also be demonstrated with a correlation diagram between the respective photoelectron bands of ethene and hydrogene chalcogenides (Figure 5). The ionization energy of ethene is 10.51 eV, the energies of the lone pair in H_2O, H_2S, and H_2Se are 12.62, 10.47, and 9.88 eV, respectively.[18,19] As a consequence, while the first band of vinyl alcohol mainly belongs to the double bond, the same in etheneselenol is of lone pair character with a considerable mixing with the double bond. Since the ionization energy of the double bond and the sulfur lone pair is almost the same, the largest interaction is expected in ethenethiol.

Figure 6 was constructed to study the correlation of ionization energies of selenocyanates. The similarity of this diagram to Figure 4 is evident. The only difference is the appearance of the additional π_1 and $\pi_1\perp$ bands between 12 and 13 eV. The spectrum of compound **6** can be derived well as the sum of the bands of the parent molecules. In case of

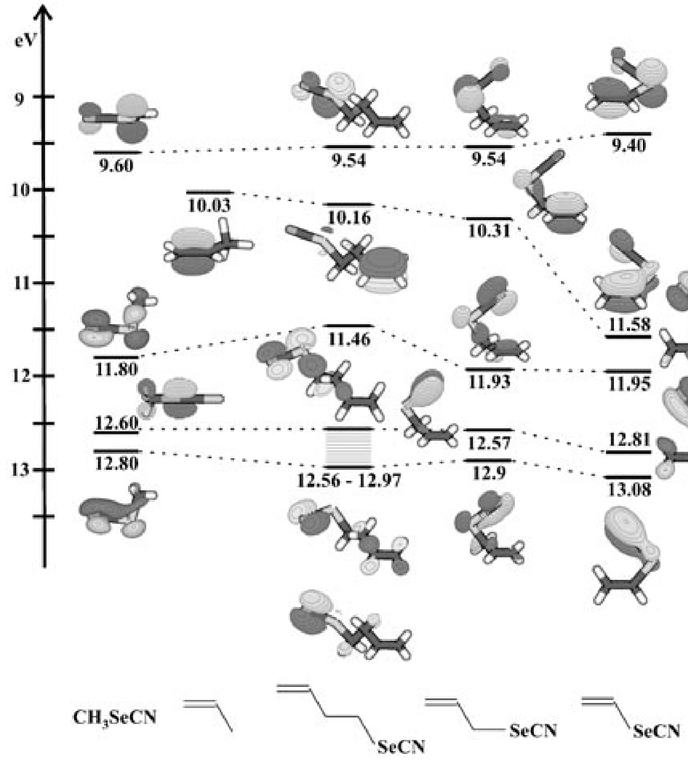


Figure 6. Correlation between the observed photoelectron bands in alkenyl selenocyanates.

the selenocyanate **5** the strong stabilization of the third band demonstrates again the appearance of the more probable **A** structure and the interaction between the C=C and the σ(Se−C) (or the $\pi_2\perp$) bonds. The band shifts in the spectrum of the vinyl derivative **4** reflects the direct interaction between the C=C π bond and the n_{Se} (or the π_2) bonds. This interaction is so strong that it shifts even the high energy π_1 band causing the exchange in the sequence of the $\pi_1\perp$ and π_1 bands.

Conclusion

Six alkenyl selenols and selenocyanates with gradually increasing distance between the selenium atom and the unsaturated group have been synthesized. Two stable vinyl and five stable allyl conformers of both series have been located on the potential-energy surface. The interaction of SeH and SeCN groups with the vinyl group has been investigated by using UV photoelectron spectroscopy and quantum chemical calculations. In the vinyl derivatives we clearly demonstrated a surprisingly strong direct conjugation of the selenium lone electron pair and the C=C double bond. On the other hand, in allyl position the selenium lone pair is independent of the C=C double bond, and the hyperconjugation between the Se−C bond and the double bond is the ruling effect. These findings were supported by the comparison of the geometry and stability of the different conformations as well as the photoelectron spectra.

The extension to the synthesis, spectroscopic characterization, and quantum chemical calculations of other unsaturated selenols and selenocyanates is currently under progress in our laboratories.

Experimental Section

Caution: *Selenols and selenocyanates are malodorous and potentially toxic compounds. All reactions and handling should be carried out in a well-ventilated hood.*

Materials: Lithium aluminum hydride, aluminum chloride, and tetraethylene glycol dimethyl ether (tetraglyme) were purchased from Acros and used as received.

General: ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker ARX400 spectrometer and ^{77}Se (52.7 MHz) on a Bruker AC300C spectrometer. HRMS (high-resolution mass spectrometry) experiments were performed on a Varian MAT 311 instrument.

He I photoelectron spectra were recorded on an instrument described earlier.[20] The resolution at the Ar $^2P_{1/2}$ line was 40 meV during the measurements. For internal calibration the N_2 and the He^+ peaks were used.

Quantum chemical calculations were performed for all the investigated molecules by the Gaussian 98 program package.[21] All of the structures were optimized at the MP2/cc-pVTZ and the B3LYP/cc-pVTZ levels of theory. The stationary points were characterized by second-derivative calculations using the same model chemistry. The relative energies were corrected using the zero-point vibrational energies. To interpret the PE spectra we proceeded in two ways. We compared the shape and position of the bands to those of related molecules whose PE bands have been assigned, and we compared the recorded vertical ionization energies with quantum chemical results obtained at the ROVGF/cc-pVTZ level of theory on the optimized geometry. For the comparison we also carried out single-point HF/cc-pVTZ calculations, on the geometries obtained above. The validity of Koopmans' theory was proved by the excellent correlation between the calculated and observed ionization energies ($R^2 = 0.98$ for selenols, 0.96 for selenocyanates).

Preparation of compounds 1–6: The synthesis of the methyl ester of selenocyanic acid,[22] and compounds **2**, **3**, **5**, and **6** were performed as previously reported.[12] Compounds **2**, **3**, and methaneselenol[23] were selectively trapped in a cooled cell (−90 °C, −70 °C, and −120 °C, respectively) equipped with stopcocks. At the end of the reaction, this cell was disconnected from the vacuum line and attached to the PE spectrometer. Methaneselenol was obtained in a 74 % yield.

Vinyl ester of selenocyanic acid (4): The vinyl Grignard reagent diluted in THF (0.1 mol, 1 M) was introduced into a 250 mL three-necked round-bottomed flask equipped with a stirring bar and a nitrogen inlet. The flask was immersed in a cold bath (−10 °C) and selenium powder (7.9 g, 0.1 mol) was added by portions. At the end of the addition, the reaction mixture was allowed to warm to room temperature and stirred for 30 min. Cyanogen bromide (10.6 g, 0.1 mol) diluted in THF (50 mL) was introduced into another 250 mL three-necked round-bottomed flask equipped with a stirring bar, a dropping funnel and a nitrogen inlet, and the flask was then immersed in a cold bath (−40 °C). The reaction mixture containing the selenolate was added dropwise. At the end of the addition the flask was allowed to warm to room temperature and stirred for 30 min. The reaction mixture was taken up in diethyl ether/water (3 × 50 mL). The organic phases were combined and dried over $MgSO_4$. After filtration, the solvents were removed under vacuum and compound **4** was purified by distillation in vacuum ($bp_{0.1}$ 35 °C). Yield : 71 %. Compound **4**

can be kept in a freezer (−20 °C) for several months without decomposition. ^{77}Se NMR (57.2 MHz, $CDCl_3$): $\delta = 305.0$ ppm; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.93$ (dd, ^3J(H,H) = 16.3 Hz, ^2J(H,H) = 1.8 Hz, 1 H; HC*H*), 6.18 (dd, ^3J(H,H) = 8.9 Hz, ^2J(H,H) = 1.8 Hz , 1 H; *H*CH), 6.56 ppm (ddd, ^3J(H,H) = 16.3 Hz, ^3J(H,H) = 8.9 Hz, ^2J(Se,H) = 18.3 Hz, 1 H; CH). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 99.9$ (s, CN), 117.1 (d, ^1J(Se,C) = 94.8 Hz, C−Se), 124.6 (t, CH_2); IR: $\tilde{\nu} = 3061.5$ (C=C−H), 2153.0 (CN), 1588.6 cm^{-1} (C=C); HRMS: calcd for $C_3H_3N^{80}Se$: 132.9431; found: 132.944; elemental analysis calcd (%) for C_3H_3NSe (132.02): C 27.29, H 2.29, N 10.61; found: C 27.09, H 2.38, N 10.33.

Etheneselenol (1):[13] $LiAlH_4$ (0.1 g, 2.4 mmol) and dry tetraglyme (20 mL) were introduced into a 50 mL two-necked flask equipped with a stirring bar and a nitrogen inlet. The flask was immersed in a cold bath (−30 °C) and aluminum chloride (1.0 g, 7.5 mmol) was added in portions. The reaction mixture was allowed to warm to −10 °C and stirred for 5 min. Compound **4** (390 mg, 3.0 mmol) diluted in dry tetraglyme (10 mL) was then added dropwise in about 5 min and the mixture was stirred for 5 min at −10 °C.

Succinic acid (2.36 g, 20 mmol) and tetraglyme (20 mL) were introduced into a 100 mL two-necked round bottomed flask equipped with a stirring bar and a septum. The flask was attached to a vacuum line equipped with two cells. The flask was degassed and then immersed in a cold bath (−10 °C). The mixture containing the aluminum selenolate was slowly added with a syringe through the septum into the flask containing the succinic acid. During and after the addition, selenol **1** was distilled off in vacuo (10^{-1} mbar) from the reaction mixture. The first trap cooled at −60 °C removed selectively the less volatile products, and compound **1** was condensed in the second trap equipped with two stopcocks and cooled at −100 °C. At the end of the reaction, this second cell was disconnected from the vacuum line by stopcocks and adapted to the PE spectrometer. Yield 66 %.

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