

Allenyl and Alkynyl Selenols and Selenocyanates. Synthesis, Spectroscopic Characterization, and Quantum Chemical Study

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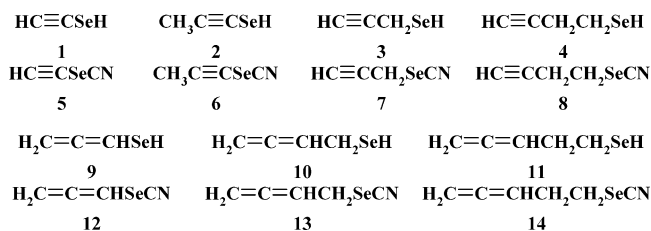
Allenyl and alkynyl selenols and selenocyanates with gradually increasing distance between the selenium atom and the unsaturated group have been synthesized and studied by photoelectron spectroscopy and quantum chemical calculations. In the triple-bonded derivatives **1**, **2**, **5**, and **6** (1-alkynylselenium derivatives), an enhanced conjugative interaction was observed, which results in a considerable (0.12–0.13 Å) Se–C bond shortening. In the propargyl **3** and **7** and homoallenyl derivatives **10** and **13** a slight but readily well observable hyperconjugation effect could be found. In the case of allenyl selenium derivatives **9** and **12** both effects are in operation, which result in a moderate Se–C bond shortening. With the previously reported study of alkenyl selenium derivatives, the type and extent of the interaction between the SeH or SeCN group and an unsaturated moiety (alkenyl, allenyl, or alkynyl substituent) are now completely clarified.

Introduction

The primary propadienyl (allenyl) and 1-alkynyl compounds bearing a group 16 heteroatom have received only limited study. Although the allenic alcohols have been clearly identified,¹ the synthesis of allenylthiols, allenylselenols, or allenyltellurols has not been reported to date. Ethynol,² ethynethiol,³ and ethyne-selenol compounds⁴ were characterized only at very low temperature, in the solid phase. This lack of information about sulfur derivatives is surprising. In the case of selenols, although alkyl and arylselenols have been known since the end of the 19th century, few functionalized derivatives have been prepared during the last century. We recently reported the synthesis of the first vinyl-, allyl-, and propargylselenols.^{5,6} We have also studied by photoelectron spectroscopy and quantum chemical calculations six alkenyl selenols and selenocyanates (vinyl, allyl, and homoallyl compounds) with gradually increasing distance between the selenium atom and the C=C bond.⁷ The interactions of SeH and SeCN groups with a vinyl group have been investigated, and in the vinyl derivatives, we clearly demonstrated a surprisingly strong direct conjugation of the selenium lone electron pair and the C=C double bond. However, in the allylic position the selenium lone pair did not interact directly

with the C=C double bond, and hyperconjugation between the Se–C bond and the C=C double bond was found as 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 two cumulative CC double bonds of allenyl derivatives or the two π orbitals of the CC triple bond of alkynyl compounds dramatically modify the properties of these molecules compared to the alkenyl species. The aim of the present work was the extension of our previous research to the corresponding allenyl and alkynyl selenium derivatives, thus completing our group 16 studies. We studied the structural and electronic properties of several allenyl and alkynyl selenols and selenocyanates in order to clarify the type and extent of the interaction between the selenium atom and the C=C or C \equiv C bond in these molecules.



Results and Discussion

1. Synthesis of Alkynyl- and Allenylselenols. The synthesis of alkynyl selenium derivatives **3**, **4**, **7**, and **8** has already been reported.⁶ We synthesized the first 1-alkynylselenocyanate, the 1-propynylselenocyanate **6**, by extension of the synthesis of 1-alkynylthiocyanates reported by Brandsma.⁸ The reaction of selenium powder with the magnesium salt of the alkyne was followed by the addition of cyanogen bromide on the formed

(8) Meijer, J.; Brandsma, L. *Rec. Trav. Chim. Pays-Bas* **1971**, *90*, 1098–1100.

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[†] Sciences Chimiques de Rennes, UMR 6226 CNRS-ENSCR.

[§] Budapest University of Technology and Economics.

(1) Hakiki, A.; Ripoll, J.-L.; Thuillier, A. *Bull. Soc. Chim. Fr.* **1985**, 911–920.

(2) Hochstrasser, R.; Wirz, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 181–183.

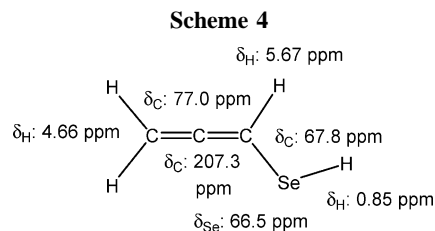
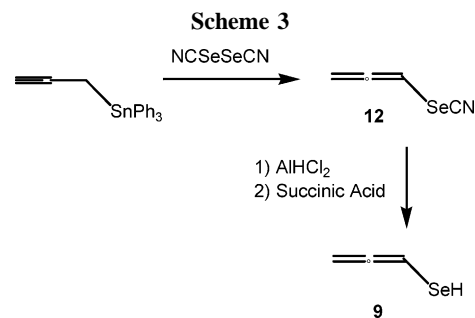
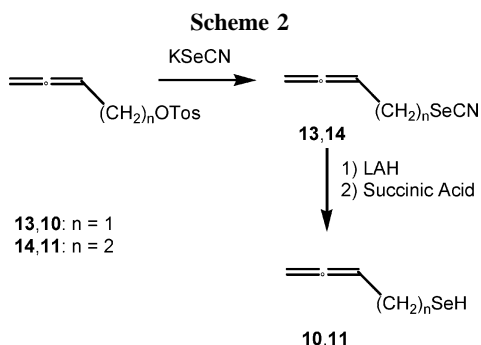
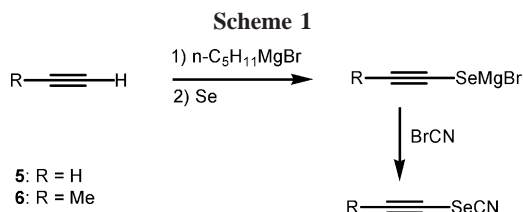
(3) Krantz, A.; Laureni, J. *J. Am. Chem. Soc.* **1974**, *96*, 6768–6770.

(4) Laureni, J.; Krantz, A.; Hajdu, R. *A. J. Am. Chem. Soc.* **1976**, *98*, 7872–7874.

(5) Guillemin, J.-C.; Bouayad, A.; Vijaykumar, D. *Chem. Commun.* **2000**, 1163–1164.

(6) Riague, El H.; Guillemin, J.-C. *Organometallics* **2002**, *21*, 68–73.

(7) Bajor, G.; Veszprémi, T.; Riague, El H.; Guillemin, J.-C. *Chem. – Eur. J.* **2004**, *10*, 3649–3656.



selenolate (Scheme 1). This compound is much more kinetically unstable than the sulfur derivatives. We also synthesized by the same approach the simplest derivative, the ethynylselenocyanate **5**, which is unstable in the reaction mixture above $-30\text{ }^{\circ}\text{C}$. Characterization of **5** was performed only by ^1H and ^{13}C NMR spectroscopy of the crude mixture.

In the case of allenyl derivatives, we synthesized compounds **13** and **14** by reaction of the corresponding tosylate^{9,10} on potassium selenocyanate. The synthesis of selenol **11** was easily performed by addition of LAH to compound **14** followed by addition of the formed mixture to a suspension of succinic acid in tetraglyme in a vacuum line. The homoalleneselenol **10** was prepared by the same approach. It presents a kinetic instability under an atmosphere of dinitrogen and at room temperature comparable with that of another β,γ -unsaturated selenol, 2-propeneselenol (Scheme 2).⁶ All these new compounds were characterized by ^1H , ^{13}C , and ^{77}Se NMR spectroscopy and HRMS (high-resolution mass spectrometry). NMR chemical shifts are typical of allenyl compounds and of β,γ - (**10**, **13**) or γ,δ - (**11**, **14**) unsaturated selenols, respectively.⁷

Allenyl compounds **12** and **9** were unambiguously the most difficult allenyl selenium derivatives to prepare. Selenocyanogen (NCSeseCN)¹¹ was prepared by addition of bromine on silver selenocyanate. Reaction of this compound with propargyltriphenylstannane led to the selenocyanate **12**, which can be purified by distillation in vacuo. However the presence of small amounts of propargylselenocyanate **7** cannot be completely avoided, and the proportion of the latter increased on standing at room temperature. The chemoselective reduction of **12** to **9** cannot be performed by LAH, this one leading to the formation of allylselenol.⁶ As already reported to prepare vinylselenol,⁷ the use of AlHCl_2 as reducing agent allowed the synthesis of α,β -unsaturated selenol, and the allenylselenol **9** was prepared by this approach (Scheme 3). The structure of this basic compound was determined by ^1H , ^{13}C , and ^{77}Se NMR spectroscopy (Scheme 4). ^1H and ^{13}C NMR data are typical of an allenyl derivative. The ^1H NMR chemical shift of the hydrogen on the selenium atom and the ^{77}Se NMR chemical shift are quite

similar to those of the vinylselenol.⁵ The molecular ion of **9** was observed by HRMS. The reduction reaction with AlHCl_2 as reducing agent was also applied to 1-propynylselenocyanate **6** but led to only 1-propeneselenol; we were not able to find a weaker reducing agent.

Thus, this study allowed the first preparation of various allenylselenols and allenylselenocyanates and provides a pathway to 1-alkynylselenocyanates.

2. Structures. The calculated structural parameters of the investigated compounds are compiled in Tables 1S and 2S in the Supporting Information. All the stable conformers found can be seen in Figures 1 and 2. The difference between the calculated MP2 and B3LYP data is a few hundred angstroms. The MP2 method generally gives somewhat longer multiple bonds and somewhat shorter Se–C bonds than the DFT method.

The triple-bonded compounds (**1**–**8**) reflect the expected geometrical effects. The calculated C–Se bond lengths in **1**, **2**, **5**, and **6** indicate a strong interaction between the π system and the selenium lone pair. This is understandable, since in the α position the selenium lone pair is able to interact with one of the π bonds. As a consequence, the C≡C bond slightly elongates (1.214 Å in propyne, 1.217 Å in **2**) and the C–Se bond considerably shortens (1.951 Å in methaneselenol, 1.819–1.824 Å in **1**, **2**, **5**, and **6**). The bond shortening in the vinyl derivatives is about 0.06 Å and in the alkynyl compounds it is 0.12–0.13 Å, indicating an enhanced conjugation effect.⁷ The opposite geometrical effect is observed in the β position. The hyperconjugative interaction elongates the C–Se bond (1.961 Å in **3a**), while the C≡C bond is almost unchanged. This effect is the same as we found in the vinyl derivatives. No considerable geometrical effect can be observed in the 3-butyne-selenol **4** and 3-butyne-selenocyanate **8** molecules.

Two minima were found on the potential surface of both propargyl (**3**, **7**) and allenyl (**9**, **12**) derivatives (Figures 1 and 2, Tables 1 and 2). The energy difference between them is only a few tenths of kcal mol^{-1} . The rotational barrier is small, only 0.98, 1.68, 1.21, and 1.31 kcal/mol , respectively. While the most stable propargylselenocyanate conformation is the C_s symmetric **7a**, the most stable propargylselenol is the out-of-plane **3b**.

In allene the two cumulative C=C bonds are obviously equal (1.308 Å experimental value,¹² 1.308 Å at the MP2/cc-pVTZ

(9) Wright, M. W.; Smalley, T. L., Jr.; Welker, M. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 6777–6791.

(10) Coates, R. M.; Senter, P. D.; Baker, W. R. *J. Org. Chem.* **1982**, *47*, 3597–3607.

(11) Meinke, P. T.; Krafft, G. A.; Guram, A. *J. Org. Chem.* **1988**, *53*, 3632–3634.

(12) Yasuhiro, O.; Satoshi, Y.; Munetaka, N.; Kozo, K. *J. Phys. Chem.* **1987**, *91* (18), 4696–4700.

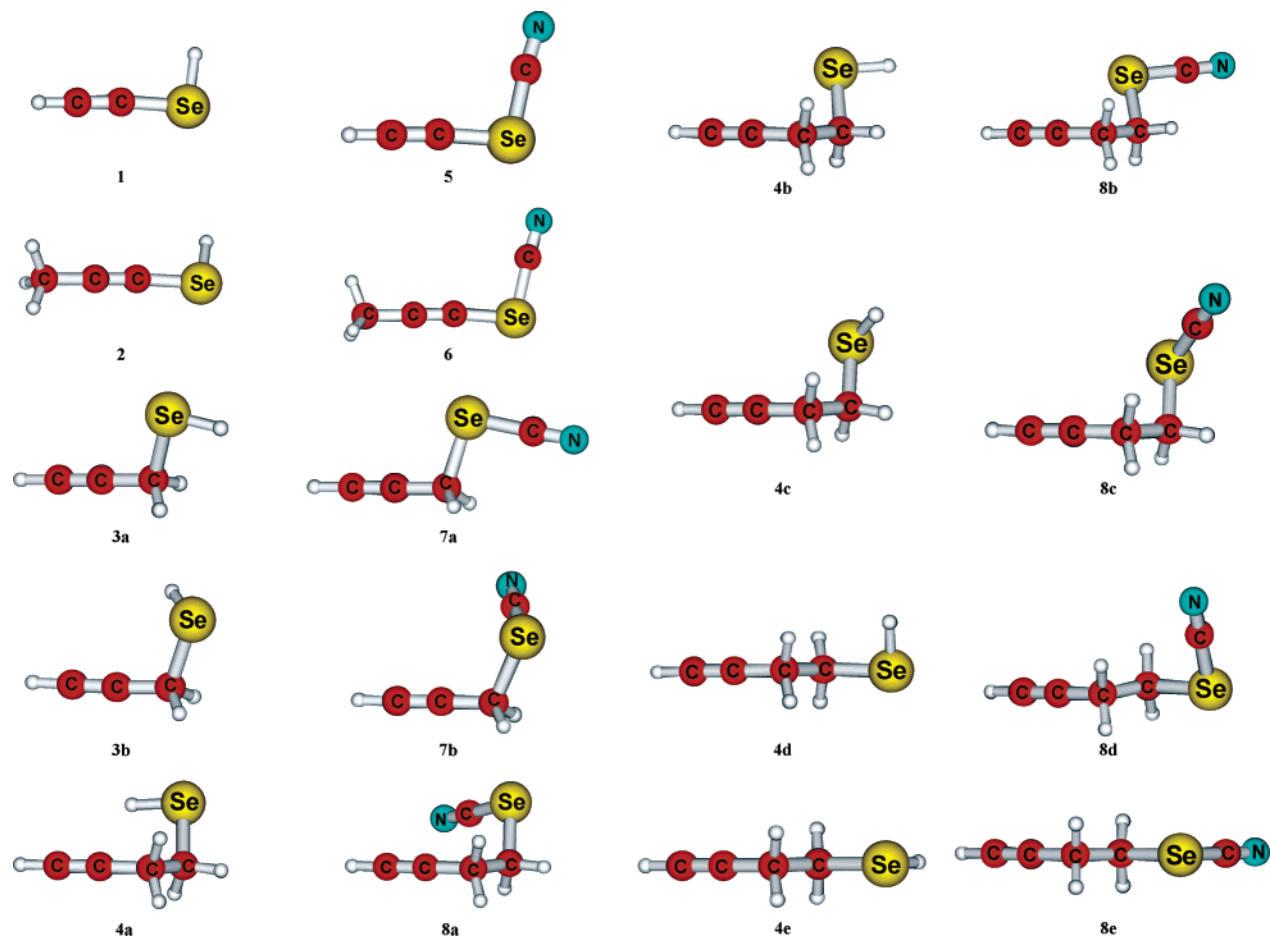


Figure 1. Stable alkynyl selenols and selenocyanates.

Table 1. Calculated Total Energies (au) and Relative Energies (kcal/mol) of Alkynyl Selenols and Selenocyanates

molecule	conformation	E_{tot}		E_{rel}	
		MP2/cc-pVTZ	B3LYP/cc-pVTZ	MP2	B3LYP
HC≡CSeH	1	-2477.2596584	-2478.9927807		
CH ₃ C≡CSeH	2	-2516.4910379	-2518.3325294		
HC≡CCH ₂ SeH	3a	-2516.4842416	-2518.3257321	0.47	0.30
	3b	-2516.4849834	-2518.3263176	0.00	0.00
HC≡CCH ₂ CH ₂ SeH	4a	-2555.7109549	-2557.6556205	0.00	0.48
	4b	-2555.7085183	-2557.6536253	1.53	1.58
	4c	-2555.7089803	-2557.6542311	1.24	1.23
	4d	-2555.7103084	-2557.6562367	0.41	0.00
	4e	-2555.7088444	-2557.6548521	1.32	0.76
HC≡CSeCN	5	-2569.3275912	-2571.2485534		
CH ₃ C≡CSeCN	6	-2608.5609967	-2610.5905721		
HC≡CCH ₂ SeCN	7a	-2608.5596942	-2610.5893310	0.00	0.00
	7b	-2608.5593235	-2610.5881576	0.23	0.72
HC≡CCH ₂ CH ₂ SeCN	8a	-2647.7845470	-2649.9165603	1.26	1.98
	8b	-2647.7849886	-2649.9181579	0.98	1.04
	8c	-2647.7864460	-2649.9189610	0.07	0.51
	8d	-2647.7865521	-2649.9198169	0.00	0.00
	8e	-2647.7837779	-2649.9178786	1.74	1.21

level). In **11** and **14**, where the distant selenium has only a negligible effect, the double-bond lengths and the C–Se distances are close to the values found in the parent compounds. In 2,3-butadieneselenol **10** and 2,3-butadienylselenocyanate **13** the slight interaction between the C=C bond and the C–Se σ bond is demonstrated by the elongation of the C–Se distance.

In the case of allenyl compounds (**9**, **12**) the out-of-plane **a** is a planar syn conformer (the planarity of the molecule refers only to the skeleton atoms). While in the (anti) **b** conformer the (Se)–H and the (Se)–CN groups are out of the molecular plane. The H–C–Se–H and the H–C–Se–C dihedral angles are between 51° and 60°. Studying the possible interactions,

we should be aware of the fact that selenium is in an allyl position to the first double bond but in a vinyl position to the second one. The perpendicular symmetry of the two double bonds is also favorable for conjugative and hyperconjugative interactions; therefore, both effects in the same molecule are expected. The two different factors cause, however, opposite geometrical effects. The Se–C bond could be shorter because of the lone pair interaction and could be longer because of the hyperconjugation. The result of the competing effects is a weaker bond shortening than was observed in vinylselenol.⁷

Five stable conformers were found in both 3-butenyl and homoallenyl derivatives (**4**, **8**, **10**, and **13**). Three of them (**4a**–

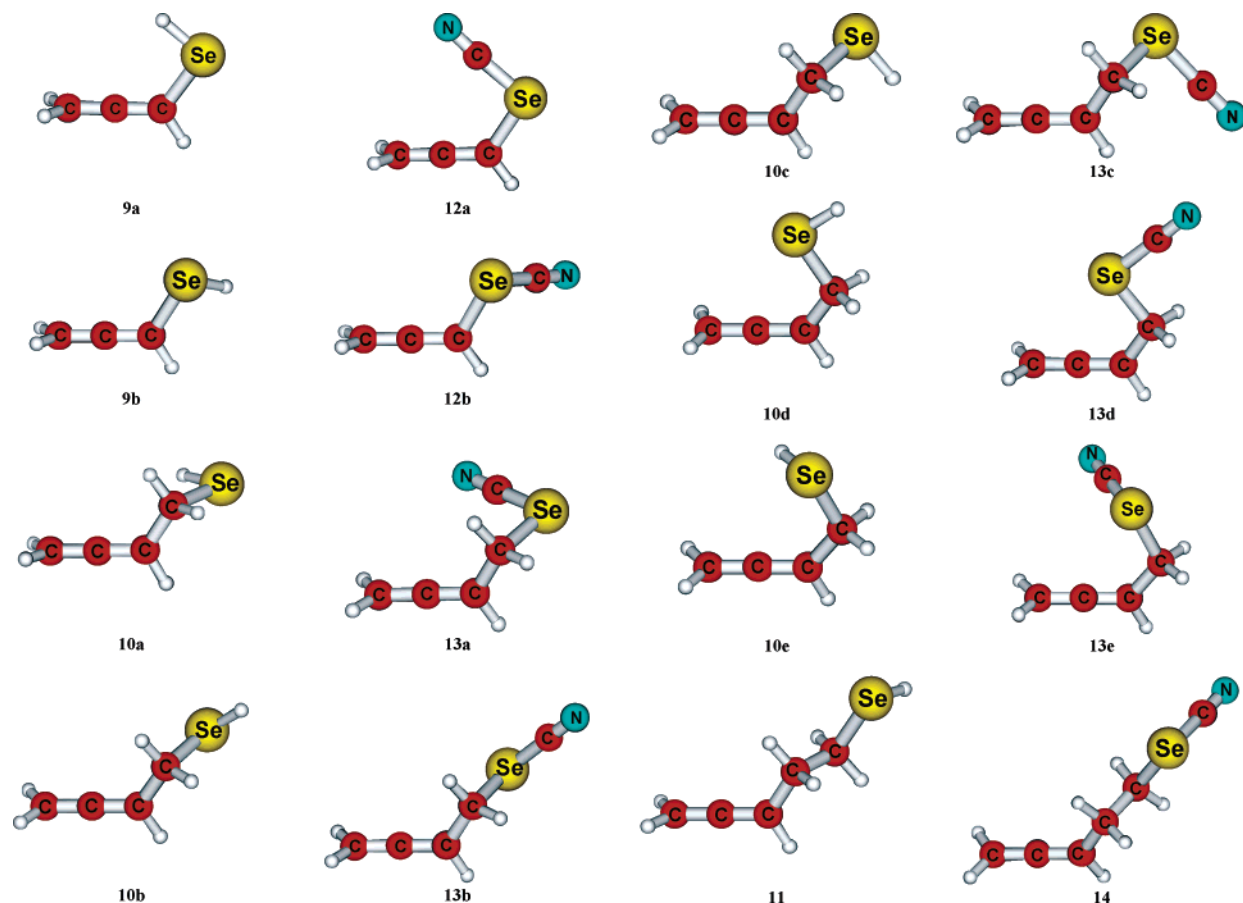


Figure 2. Stable allenyl selenols and selenocyanates.

Table 2. Calculated Total Energies (au) and Relative Energies (kcal/mol) of Allenyl Selenols and Selenocyanates

molecule	conformation	E_{tot}		E_{rel}	
		MP2/cc-pVTZ	B3LYP/cc-pVTZ	MP2	B3LYP
$\text{H}_2\text{C}=\text{C}=\text{CHSeH}$	9a	-2516.4823528	-2518.3340933	0.00	0.06
	9b	-2516.4820971	-2518.3339200	0.16	0.00
$\text{H}_2\text{C}=\text{C}=\text{CHCH}_2\text{SeH}$	10a	-2555.7073792	-2557.6647432	0.00	0.00
	10b	-2555.7058573	-2557.6634744	0.96	0.68
	10c	-2555.7058226	-2557.6635145	0.98	0.65
	10d	-2555.7045364	-2557.6603337	1.78	2.56
	10e	-2555.7047401	-2557.6604379	1.66	2.40
$\text{H}_2\text{C}=\text{C}=\text{CHCH}_2\text{CH}_2\text{SeH}$	11	-2594.9282042	-2596.9907597		
$\text{H}_2\text{C}=\text{C}=\text{CHSeCN}$	12a	-2608.5563443	-2610.5947851	0.00	0.76
	12b	-2608.5561758	-2610.5960959	0.11	0.00
$\text{H}_2\text{C}=\text{C}=\text{CHCH}_2\text{SeCN}$	13a	-2647.7848326	-2649.9286350	0.00	0.00
	13b	-2647.7823975	-2649.9283147	1.53	0.21
	13c	-2647.7829392	-2649.9282043	1.19	0.27
	13d	-2647.7815098	-2649.9252084	2.09	1.99
	13e	-2647.7817008	-2649.9239744	1.97	2.67
	14	-2687.0043156	-2689.2550547		

c, **8a–c** and **10a–c**, **13a–c**) are when the selenium atom is out of the plane of the 3-butenyl or homoallenyl group (referred to as **A** conformations). These structures differ only by the direction of the Se–H or Se–CN bond. In the minima **4d,e**, **8d,e** and **10d,e**, **13d,e** (**B** conformations) the selenium atom is situated in the plane of the butynyl or homoallenyl group. Hyperconjugation can be realized only in **A**-type conformers.

While in the case of homoallenyl compounds and 3-butenylselenocyanate **8** the **A** conformations are the most stable, in the case of butyneselenol **4** the relative stability depends on the method of calculation.

In **11** and **14** it can be assumed that the interaction with the distant selenium atom is negligible and only the inductive (and some steric) effect of the alkadienyl group is responsible for

the geometrical and spectroscopic properties. Therefore, only one conformer, which was assumed to be one of the most stable ones, was calculated.

3. Photoelectron Spectroscopy. The observed UV photoelectron spectra of the investigated compounds are seen in Figures 3 and 4. The position of the most important photoelectron bands and the calculated vertical ionization energies using the ROVGF method (for the most stable conformers) and Koopmans' theorem (for all conformers) are collected in Tables 3 and 4.

The outer valence Green's function method^{13,14} uses a third-order approximation scheme, and using a proper basis set in general excellent agreement with the experimental data can be observed^{15,7} (in our calculations $R^2 = 0.99$ for alkynyl deriva-

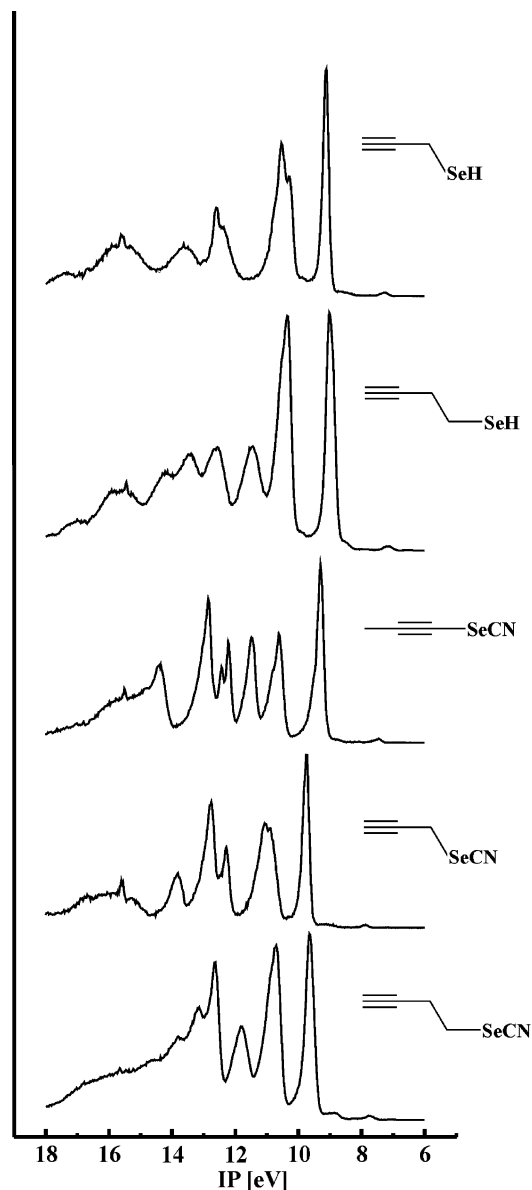


Figure 3. Photoelectron spectra of alkynyl selenols and selenocyanates.

atives and $R^2 = 0.97$ for allenyl derivatives). The agreement with the MO energies is somewhat worse, but a good linear correlation with the PE bands suggests the validity and applicability of Koopmans' theorem ($R^2 = 0.98$ for alkynyl compounds and 0.97 for allenyl compounds). As is well known, the calculated IE using Koopman's theorem gets worse for higher IEs (the largest difference is 2.1 eV in our calculations). In the case of the ROVGF results the average deviation is 0.1 eV for alkynyl compounds (maximum deviation 0.4 eV) and 0.2 eV for allenyl compounds (maximum deviation 0.7 eV).

(13) Cederbaum, L. S.; Domcke, W. *Adv. Chem. Phys.* **1977**, *36*, 205–344. von Niessen, W.; Schirmer, J.; Cederbaum, L. S. *Comput. Phys. Rep.* **1984**, *1*, 57–125.

(14) Zakrzewski, V. G.; von Niessen, W. *J. Comput. Chem.* **1993**, *14*, 13. Zakrzewski, V. G.; Ortiz, J. V. *Int. J. Quantum Chem.* **1995**, *53*, 583–590. Zakrzewski, V. G.; Ortiz, J. V. *Int. J. Quantum Chem.* **1994**, *28*, 23–27.

(15) Trofimov, A. B.; Schirmer, J.; Kobychov, V. B.; Potts, A. W.; Holland, D. M. P.; Karlsson, L. *J. Phys. B: At. Mol. Opt. Phys.* **2006**, *39*, 305–329. Sun, S.; Zeng, Y.; Meng, L.; Zheng, S.; Wang, D.; Mok, D. K.; Chau, F. *J. Electron Spectrosc.* **2005**, *142*, 261–264. Qiao, Z.; Sun, S.; Sun, Q.; Zhao, J.; Wang, D. *J. Chem. Phys.* **2003**, *119*, 7111–7114. Potts, A. W.; Trofimov, A. B.; Schirmer, J.; Holland, D. M. P.; Karlsson, L. *Chem. Phys.* **2001**, *271*, 337–356

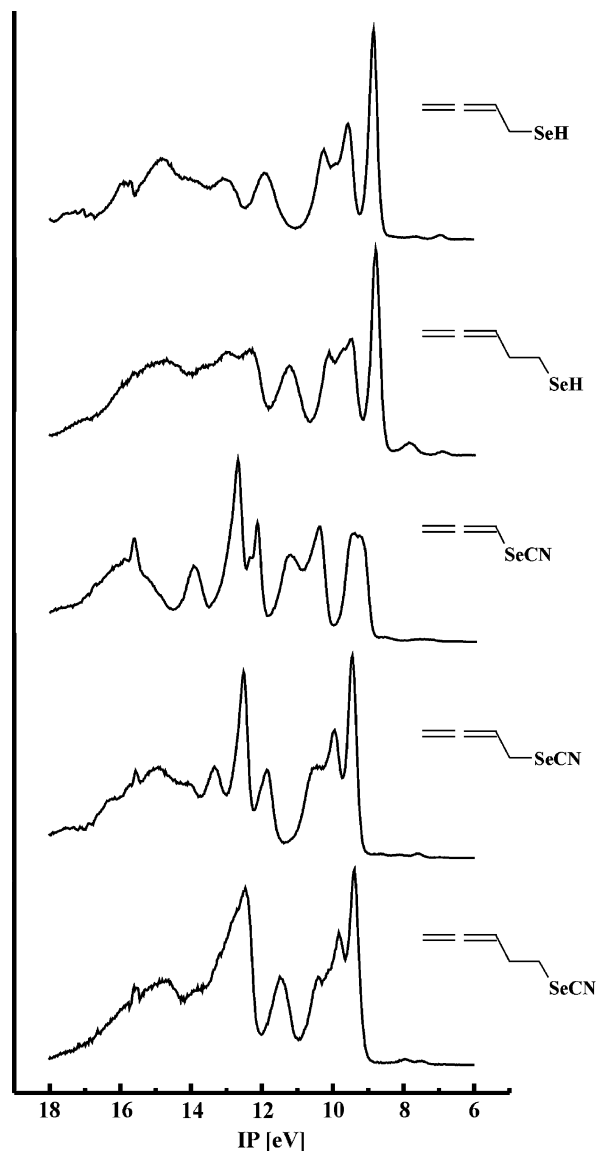


Figure 4. Photoelectron spectra of allenyl selenols and selenocyanates.

The spectra of allenyl and alkynyl selenols can be characterized by their four 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. A single Se–C bond and a triple C \equiv N bond can be assumed. In this case the appearance of two new bands (the C \equiv 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-center 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 CH₃–NCS_e), the perpendicular MO pairs are degenerate. In the case of the strongly bent R–SeCN, theoretically the appearance of all four π bands is expected. However, the selenium lone pair in the SeCN group is part of a π system, and the σ (Se–C)orbital is also part of the perpendicular π system. As a summary, only two additional bands are expected in the low-energy spectrum region.

Table 3. Experimental and Calculated^a Ionization Energies [eV] of Alkynyl Selenols and Selenocyanates

no.	molecule	IE _{exptl}	IE _{calcd}					assignment	
			a	b	c	d	e		
1	HC≡CSeH		9.30 (9.14)					$n_{\text{Se}} - \pi$	
			11.11 (10.71)					π	
			12.52 (11.80)					$n_{\text{Se}} + \pi$	
			13.97 (13.49)					$\sigma(\text{C} - \text{Se})$	
2	HC≡CSeH		8.90 (8.63)					$n_{\text{Se}} - \pi$	
			10.52 (9.99)					π	
			12.00 (11.25)					$n_{\text{Se}} + \pi$	
			13.63 (13.12)					$\sigma(\text{C} - \text{Se})$	
3	HC≡CCH ₂ SeH	9.09	9.38	9.38 (9.11)				n_{Se}	
		10.28	10.67	10.57 (10.24)				π	
		10.58	11.00	10.94 (10.52)				π	
		12.4–12.6	12.55	12.86 (12.48)				$\sigma(\text{C} - \text{Se})$	
4	HC≡CCH ₂ CH ₂ SeH	9.02	9.17 (8.90)	9.12	9.18	9.31 (9.07)	9.27	n_{Se}	
		10.34	10.76 (10.39)	10.70	10.61	10.77 (10.36)	10.79	π	
		10.3–10.5	10.86 (10.47)	10.81	10.74	10.81 (10.40)	10.83	π	
		11.55	11.78 (11.40)	11.81	11.87	12.06 (11.71)	11.95	$\sigma(\text{C} - \text{Se})$	
		12.58	13.62 (12.95)	13.64	13.59	13.72 (12.99)	13.97	σ	
5	HC≡CSeCN		10.06 (9.75)					$\pi - \pi_2$	
			12.03 (11.47)					π	
			12.94 (11.99)					$\pi + \pi_2$	
			13.38 (12.56)					$\pi_2 \perp$	
			14.62 (13.49)					π_1	
			15.26 (13.61)					$\pi_1 \perp$	
6	CH ₃ C≡CSeCN	9.30	9.64 (9.24)					$\pi - \pi_2$	
		10.65	11.37 (10.50)					π	
		11.51	12.43 (11.46)					$\pi + \pi_2$	
		12.48	13.16 (12.31)					$\pi_2 \perp$	
		12.85	14.36 (13.19)					π_1	
7	HC≡CCH ₂ SeCN		12.85	15.01 (13.42)				$\pi_1 \perp$	
			9.75	10.15 (9.63)	10.13				π_2
			10.85	11.24 (10.83)	11.06				π
			11.09	11.58 (11.10)	11.35				π
			12.35	13.00 (12.26)	12.96				$\pi_2 \perp$
8	HC≡CCH ₂ CH ₂ SeCN		12.79	14.10 (12.87)	14.05			π_1	
			14.40 (13.30)	14.47				$\pi_1 \perp$	
			13.81	15.39 (13.53)	15.31				σ
			9.65	9.91	9.89	9.95	10.07 (9.64)	10.03	π_2
			10.69	10.91	11.20	11.02	11.09 (10.65)	11.17	π
			10.69	11.01	11.32	11.12	11.10 (10.64)	11.23	π'
			11.81	12.16	12.25	12.27	12.44 (11.85)	12.39	$\pi_2 \perp$
			12.65	13.83	13.87	13.95	14.01 (12.78)	13.96	π_1
				13.89	13.98	14.04	14.18 (13.13)	14.09	$\pi_1 \perp$

^a Regular numbers indicate the results calculated with Koopmans' theorem; numbers in parentheses indicate the OVGf results.

Since several conformers with comparable energies are possible in some cases, we should also investigate whether the spectra can originate from a mixture of all conformers or if only some of them dominate.

Figures 5 and 6 were constructed to study the correlation of ionization energies in the compounds containing a C≡C triple bond. In the spectra of **3** and **4** the position of the first band is almost unchanged. In propyne the two π -MOs are degenerate, which is revealed in the huge first band of the spectrum of the molecule.¹⁶ In **4** the degeneracy hardly split; only the small asymmetry on the second, very intense band indicates the splitting. The ionization energies are close to those of the parent compounds methaneselenol and propyne. The origin of the slight shifts of the bands is the inductive effect. In **3**, however, the C–Se bonding orbital interacts with one of the π -MOs, resulting in a slightly destabilized π orbital and a strongly stabilized C–Se orbital. This effect is indicated by the position of the second and fourth band in the spectrum. The third band attributed to the perpendicular component of the π orbital stabilized by 0.21 eV compared to propyne.

In allylselenol depending on the position of the Se–H group the interaction between the π and n_{Se} orbitals changes.⁷ In **3** and **4**, however, we could not find a significant difference in the calculated ionization energies of different conformations because of the cylindrical symmetry of the π system.

Although ethyneselenol (**1**) and 1-propyneselenol (**2**) have not been synthesized, the expected spectrum could easily be estimated on the basis of the calculations. In both molecules a huge splitting of the π bands and a strong shift of all the considered bands are expected, which indicates a strong orbital interaction. In these molecules the –SeH group is responsible for two different effects: the interaction of the Se lone pair and the hyperconjugation of the –SeH bond. Since the appropriate orbitals are practically perpendicular, they can separately interact with the respective components of the perpendicular π bonds (Figure 7). In **2** this scheme becomes more complicated with the hyperconjugation of the methyl group at the opposite side of the triple bond (Figure 7b). Compared to ethyne and propyne, the hyperconjugation of the methyl group shifts the π bands in the PES by about 1 eV (from 11.40 eV to 10.37 eV). Because of the proper symmetry, it does not split the degeneracy of the π bands. The destabilized π bands lift all the interacting orbitals in **2** by about 0.5 eV.

(16) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*; Japan Scientific Societies Press: Tokyo; Halsted Press: New York, 1981.

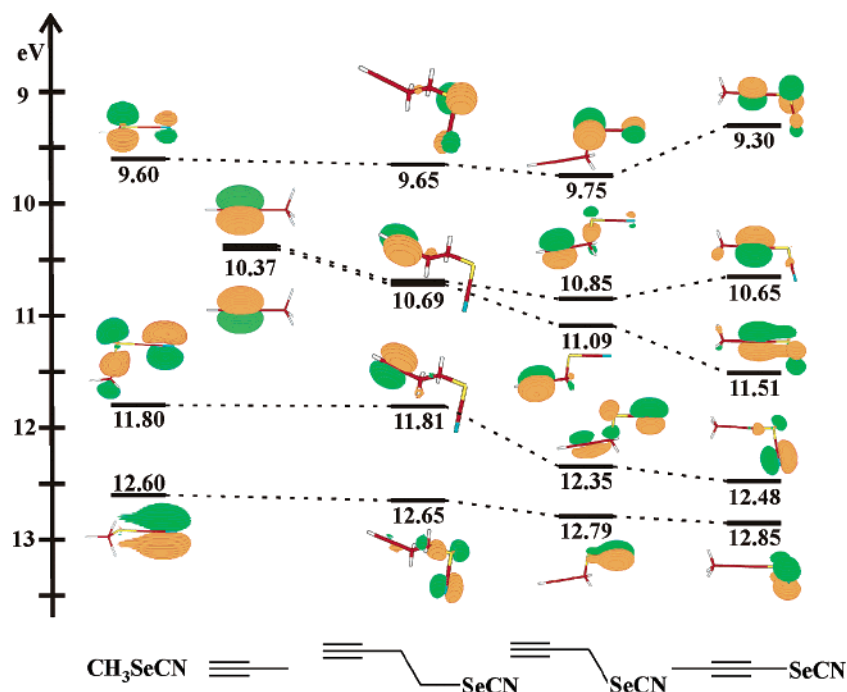


Figure 5. Correlation between the observed photoelectron bands in alkenyl selenocyanates.

Table 4. Experimental and Calculated^a Ionization Energies [eV] of Allenyl Selenols and Selenocyanates

no.	molecule	IE _{exptl}	IE _{calcd}					assignment	
			a	b	c	d	e		
9	H ₂ C=C=CHSeH		8.70 (8.47)	9.14 (8.75)				$\pi - n_{\text{Se}}$	
			10.27 (9.94)	10.41 (9.90)				$\pi \perp$	
			11.88 (11.15)	10.85 (10.51)				$\pi + n_{\text{Se}}$	
			13.08 (12.62)	13.16 (12.54)				$\sigma(\text{C} - \text{Se})$	
			14.98 (13.91)	15.36 (14.34)				σ	
10	H ₂ C=C=CHCH ₂ SeH	8.84	9.14 (8.83)	9.16	9.12	9.09	9.13	n_{Se}	
			9.54	9.99 (9.53)	9.98	9.94	10.18	10.13	π
			10.27	10.48 (9.96)	10.50	10.49	10.38	10.36	$\pi \perp$
			11.92	12.39 (11.99)	12.16	12.44	11.86	11.87	$\sigma(\text{C} - \text{Se})$
			12.87	14.12 (13.34)	14.31	13.86	13.72	13.70	σ
11	H ₂ C=C=CHCH ₂ CH ₂ SeH	8.81	9.12 (8.88)					n_{Se}	
			9.50	10.07 (9.48)				π	
			10.13	10.23 (9.84)				$\pi \perp$	
			11.24	11.75 (11.41)				$\sigma(\text{C} - \text{Se})$	
			12.3	13.66 (12.81)				σ	
			13.0	14.01 (12.86)				σ	
12	H ₂ C=C=CHSeCN	9.3	9.40 (9.05)	9.89 (9.32)				$\pi - \pi_2$	
			10.40	10.80 (10.23)	11.02 (10.43)			$\pi \perp$	
			11.24	12.20 (11.26)	11.59 (10.88)			$\pi + \pi_2$	
			12.12	12.92 (12.05)	13.02 (12.17)			$\pi_2 \perp$	
			12.69	14.24 (13.03)	13.98 (12.77)			π_1	
			13.88	14.63 (13.19)	14.68 (13.35)			$\pi_1 \perp$	
13	H ₂ C=C=CHCH ₂ SeCN	9.44	9.82 (9.27)	9.90	9.83	9.87	9.90	π_2	
			9.95	10.37 (9.71)	10.49	10.42	10.74	10.48	π
			10.46	10.77 (10.10)	11.01	10.89	10.92	10.67	$\pi \perp$
			11.85	12.57 (11.63)	12.62	12.70	12.29	12.23	$\pi_2 \perp$
			12.52	13.86 (12.61)	13.86	13.94	13.86	13.85	π_1
			13.38	14.16 (13.04)	14.10	14.28	13.99	13.99	$\pi_1 \perp$
14	H ₂ C=C=CHCH ₂ CH ₂ SeCN	9.38	9.89 (9.46)					π_2	
			9.80	10.43 (9.81)				π	
			10.35	10.67 (10.17)				$\pi \perp$	
			11.46	12.19 (11.45)				$\pi_2 \perp$	
			12.47	13.83 (12.59)				π_1	
				13.93 (12.89)				$\pi_1 \perp$	

^a Regular numbers indicate the results calculated with Koopmans' theorem; numbers in parentheses indicate the OVGf results.

For the assignment of the spectra of selenocyanates, the spectral data of methylselenocyanate and propyne were applied.^{16,17} The similarity to the spectra of selenols (Figure 6) is clear. The only difference is the appearance of the additional π bands between 12.6 and 12.8 eV (and below). According to the correlation diagram (Figure 5) the first intense band around

9.70 eV can be attributed to the π system of the SeCN group. In **6** this band appears at 9.30 eV. Considering the calculated first ionization energies of **5**, **7**, and **8**, this destabilization is caused similarly to **2** by the hyperconjugation of the methyl group. The next two bands between 10.65 and 11.51 eV can be attributed to the C \equiv C triple bond. In **6** as a result of the strong

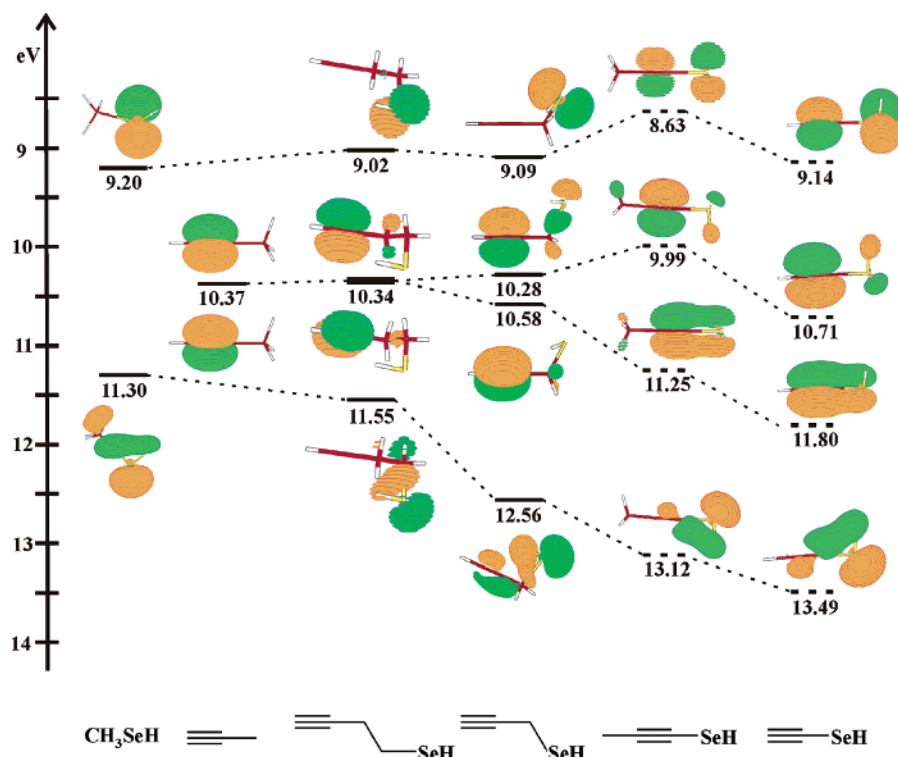


Figure 6. Correlation between the observed photoelectron bands in alkynyl selenols. As ethynylselenol (**1**) could not be measured, the OVG results (broken line) are given.

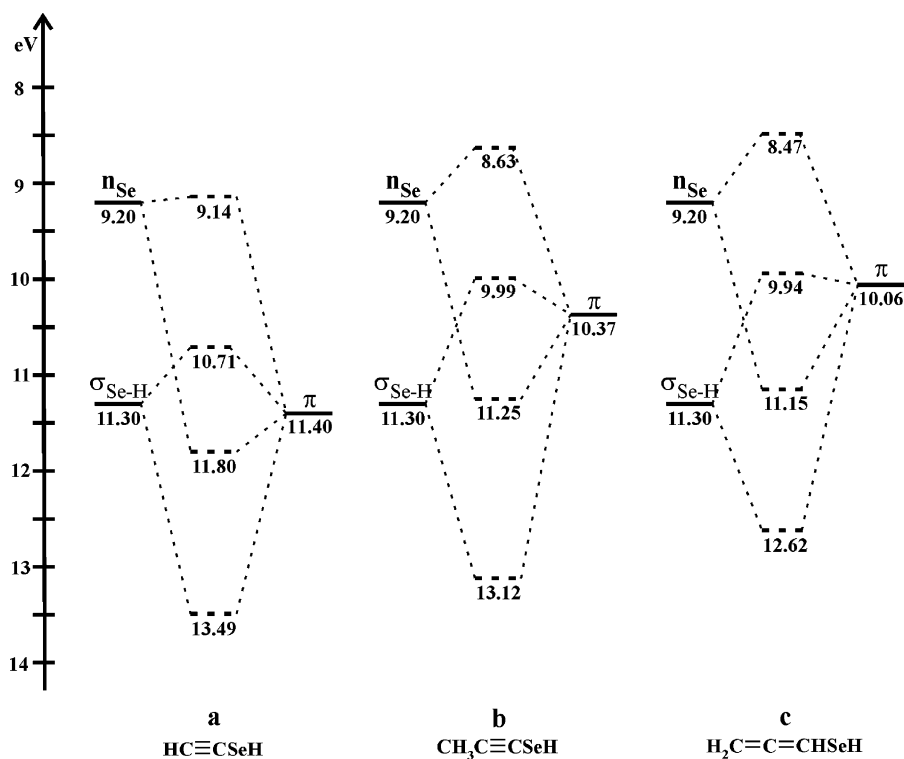


Figure 7. Correlation between the corresponding photoelectron band in (a) ethynylselenol (**1**), (b) prop-1-ynylselenol (**2**), and (c) propa-1,2-dienylselenol (**9**) compared to (a) ethyne, (b) propyne, and (c) allene and methaneselenol.

interaction between the two unsaturated parts of the molecules, the splitting is 0.86 eV.

For the assignment of the PE spectra of allenylselenols the experimental ionization energies of methaneselenol and allene were applied.^{7,16} The synthesized propa-1,2-dienylselenol (**9**) was

(17) Pasinszki, T.; Veszprémi, T.; Fehér, M.; Kovac, B.; Klasinc, L.; McGlynn, S. P. *Int. J. Quantum Chem.* **1992**, 443–453.

found to be contaminated; therefore we could not record a proper spectrum. Nevertheless, expected band positions can be seen in Figure 8, and we can compare the calculated ionization energies.

In the spectra (Figure 4) the first sharp peak belongs to the selenium lone pair, and the second and third bands can be assigned to the π system (Figure 8). The originally degenerated

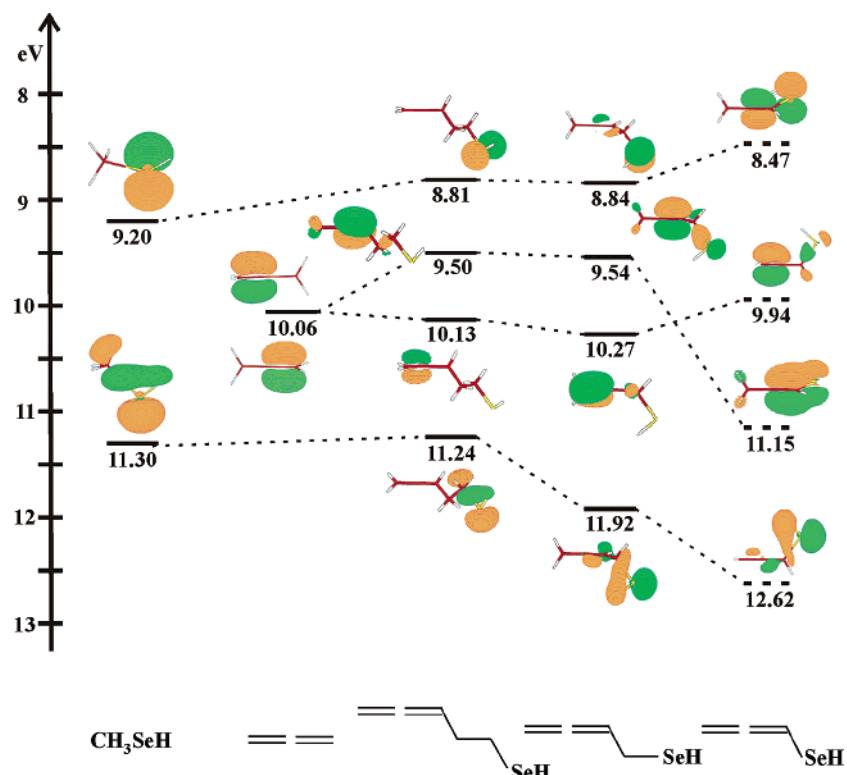


Figure 8. Correlation between the observed photoelectron bands in allenyl selenols. As propa-1,2-dieneselenol (**9**) could not be measured, the OVG results (broken line) are given.

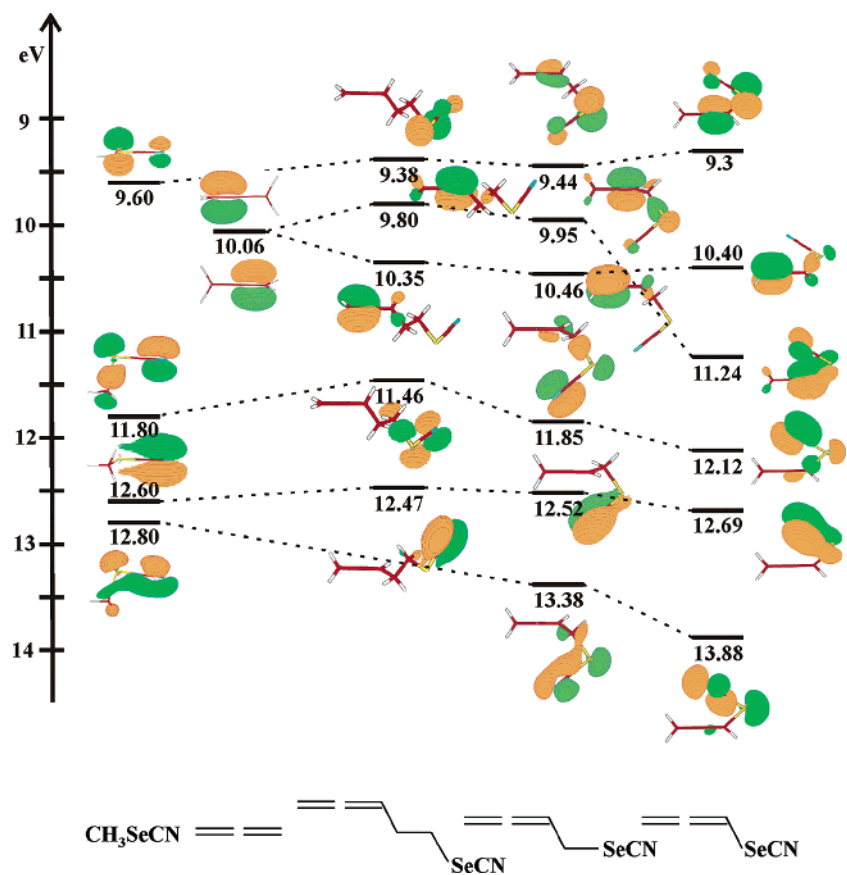


Figure 9. Correlation between the observed photoelectron bands in allenyl selenocyanates.

orbitals split in **11**, indicating some hyperconjugation effect, which increases in **10**.

Three possible effects, the conjugation between the Se lone pair and the neighboring double bond, the hyperconjugation

between the SeH bond and the nearer double bond, and the hyperconjugation between the Se–C bond and the farther double bond, complicate the spectrum of **9**. Since the Se lone pair and the Se–H bonds are perpendicular, depending on the actual

conformation, only one of them can interact with the nearer π bond. The result is the same: the destabilized first and stabilized third band. The hyperconjugation of the Se–C bond causes the stabilization of the fourth and destabilization of the second band. The total effect is similar to those found in the spectra of **1** and **2** (see Figure 7c).

Studying the difference between the observed first three ionization energies in **10** and comparing to the calculated values for the different conformers, the **A** conformation seems to be more likely than **B**.

In the spectra of allenyl selenocyanates the first intense band can be attributed to the π system of the SeCN group (Figure 9). The characteristic bands of the cumulated double bond system appear between 9.3 and 11.2 eV. The strong conjugation in **12** between the appropriate π system of the SeCN and allenyl group (π, π_2) can be explained in a similar way to that in **9**. This conjugation should result in a destabilized $\pi - \pi_2$ orbital and a stabilized $\pi + \pi_2$ orbital, which can be seen in the experimental spectrum of **12**.

Conclusion

Four alkynyl and six allenyl selenols and selenocyanates with gradually increasing distance between the selenium atom and the unsaturated group have been synthesized and characterized. The interaction of SeH and SeCN groups with the unsaturated moiety has been investigated by using UV photoelectron spectroscopy and quantum chemical calculations. In the triple-bonded derivatives **1**, **2**, **5**, and **6** we clearly demonstrated an enhanced conjugative interaction, which results in a considerable 0.12–0.13 Å Se–C bond shortening. In the triple-bonded **3** and **7** and allene derivatives **10** and **13** a slight but well observable hyperconjugation effect could be found. In the case of allenyl compounds **9** and **12** both effects are in operation, which results in a moderate Se–C bond shortening. The photoelectron spectra well demonstrate the orbital interactions. Because several unsaturated cyanates and thiols were not available, this study gives a better knowledge on orbital interactions of unsaturated selenols and selenocyanates than that reported up to now for the corresponding oxygen and sulfur derivatives.

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, succinic acid, and tetraethyleneglycol dimethyl ether (tetraglyme) were purchased from Acros and used as received. 2,3-Butadiene-1-ol, 4-methylbenzenesulfonate,⁹ 3,4-pentadiene-1-ol, and 4-methylbenzenesulfonate¹⁰ were prepared as previously reported. All the experiments at atmospheric pressure have been performed under nitrogen.

General Procedures. ¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded on a Bruker ARX400 spectrometer and ⁷⁷Se (52.7 MHz) on a Bruker AC300C spectrometer. Chemical shifts are given in ppm (δ) relative to tetramethylsilane (¹H), solvent (¹³C, CDCl₃, δ 77.0 ppm), and external Me₂Se (⁷⁷Se NMR). The NMR spectra were recorded using CDCl₃ as solvent. 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.¹⁸ The resolution at the Ar ²P_{1/2} line was 40 meV during the measurements. For internal calibration the N₂ and the

He⁺ peaks were used. Quantum chemical calculations were performed for all the investigated molecules by the Gaussian 03 program package.¹⁹ 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 comparison we also carried out single-point HF/cc-pVTZ calculations on the geometries obtained above.

Preparation of Compounds 7, 8, 3, and 4. The synthesis of selenocyanic acid, 2-propyne ester **7**, selenocyanic acid, 3-butyne ester **8**, 2-propyneselenol **3**, and 3-butyne-selenol **4** were performed as previously reported.⁶ Compounds **3** and **4** were selectively trapped in a cooled cell (−90 and −70 °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.

Selenocyanic Acid, Ethyne Ester (5). In a 250 mL flask were introduced under nitrogen magnesium (528 mg, 22 mmol) and freshly distilled THF (40 mL). 1-Bromopentane (3.3 g, 22 mmol) was added to form the Grignard reagent. In another flask containing dry THF (60 mL) cooled at −50 °C was introduced ethyne (0.68 L, 30 mmol). The Grignard reagent was then added to this solution, and the mixture was allowed to warm to room temperature. The mixture was cooled at −10 °C, and selenium powder (1.58 g, 20 mmol) was slowly 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 (2.1 g, 20 mmol) diluted in THF (20 mL) was introduced into another 250 mL 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, and the mixture was stirred at this temperature for 1 h. A sample immersed in a cold bath (−40 °C) was concentrated in vacuo and quickly analyzed by NMR spectroscopy at low temperature. Bp: 10 °C (0.1 mbar). ¹H NMR (400 MHz, CDCl₃, −40 °C): δ 3.19 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, −40 °C): δ 57.8 (s, ²J_{CH} = 49.8 Hz, C–Se); 89.2 (d, ¹J_{CH} = 255.4 Hz, HC); 95.0 (s, CN). At a temperature higher than −30 °C, a fast decrease of the signals attributed to compound **5** was observed.

Selenocyanic Acid, 1-Propyne Ester (6). In a 250 mL flask were introduced under nitrogen magnesium (528 mg, 22 mmol) and freshly distilled THF (40 mL). 1-Bromopentane (3.3 g, 22 mmol) was added to form the Grignard reagent. In another flask containing dry THF (60 mL) cooled at −50 °C was introduced propyne (0.68 L, 30 mmol). The Grignard reagent was then added to this solution, and the mixture was allowed to warm to room temperature. The mixture was cooled at −10 °C, and selenium powder (1.58 g, 20 mmol) was slowly added by portions. At the

(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Aboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(18) Veszprémi, T.; Zsombok, Gy. *Magy. Kém. Foly.* **1986**, *92*, 39–40.

end of the addition, the reaction mixture was allowed to warm to room temperature and stirred for 30 min. Cyanogen bromide (2.1 g, 20 mmol) diluted in THF (20 mL) was introduced into another 250 mL flask equipped with a stirring bar, a dropping funnel, and a nitrogen inlet, and the flask was then immersed in a cold bath ($-40\text{ }^{\circ}\text{C}$). 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 filtrated under nitrogen and kept in a freezer ($-30\text{ }^{\circ}\text{C}$). A pure sample was prepared by distillation in a vacuum line and selective trapping of compound **6** at $-40\text{ }^{\circ}\text{C}$. Yield: 63%, bp $30\text{ }^{\circ}\text{C}$ (0.1 mbar). ^1H NMR (400 MHz, CDCl_3): δ 2.09 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 5.3 (q, $^1J_{\text{CH}} = 132.5\text{ Hz}$, CH_3); 45.6 (s, $^1J_{\text{CSe}} = 160.6\text{ Hz}$ (d), C–Se); 97.1 (s, CN); 103.1 (s, $^2J_{\text{CSe}} = 29.7\text{ Hz}$, Me–C). ^{77}Se NMR (57.2 MHz, CDCl_3): δ 240.6. IR (film, cm^{-1}): 3308 (s, $\nu_{\text{C=CH}}$), 2961 (s), 2200 (s, $\nu_{\text{C=C}}$), 2164 (s, ν_{CN}), 1466 (s), 1317 (s), 1093 (s). HRMS: calcd for $\text{C}_4\text{H}_3\text{N}^{80}\text{Se}$ 144.9431, found 144.943.

Selenocyanic Acid, Propa-1,2-diene Ester (12). In a 250 mL flask were introduced, under nitrogen, potassium selenocyanate (2.5 g, 17.5 mmol) and water (60 mL). Silver nitrate (3 g, 17.5 mmol) was slowly added at room temperature. After 30 min of stirring, the solution was filtrated and silver selenocyanate, dried under vacuo, was obtained as a white solid in 92% yield (3.4 g, 16.1 mmol).¹¹

Silver selenocyanate (3.41 g, 16 mmol) diluted in benzene (20 mL) was introduced in a 100 mL flask equipped with a stirring bar, a dropping funnel, and a nitrogen inlet. The flask was cooled at $10\text{ }^{\circ}\text{C}$, and dibromine (1.28 g, 8 mmol) was then added dropwise. The mixture was stirred for 30 min, then filtrated and introduced dropwise in another flask containing prop-2-ynyltriphenylstannane (2.73 g, 7 mmol) in benzene (20 mL) at $10\text{ }^{\circ}\text{C}$. The mixture was stirred for 1 h, and water was added. The reaction mixture was taken up in diethyl ether/water ($3 \times 50\text{ mL}$). The organic phases were combined and dried over MgSO_4 . After filtration, the solvent was removed under vacuum. Selenocyanic acid, 1,2-propadiene ester **12** was purified by distillation in a vacuum line and selective trapping at $-30\text{ }^{\circ}\text{C}$. Yield: 55%, bp $40\text{ }^{\circ}\text{C}$ (0.1 mbar). ^1H NMR (400 MHz, CDCl_3): δ 5.17 (d, $^4J_{\text{HH}} = 6.1\text{ Hz}$, 2H, CH_2); 6.03 (t, $^4J_{\text{HH}} = 6.1\text{ Hz}$, $^2J_{\text{SeH}} = 26.2\text{ Hz}$, 1H, CH–Se). ^{13}C NMR (100 MHz, CDCl_3): δ 71.2 (d, $^1J_{\text{CH}} = 202.4\text{ Hz}$, $^1J_{\text{CSe}} = 89.2\text{ Hz}$, CH); 80.5 (t, $^1J_{\text{CH}} = 170.9\text{ Hz}$, CH_2); 100.7 (s, CN), 208.5 (s, C=C=C). ^{77}Se NMR (57.2 MHz, CDCl_3): δ 277.4. IR (film, cm^{-1}): 3041 (m, $\nu_{\text{C=CH}}$), 2153 (w, ν_{CN}), 1941 (s, $\nu_{\text{C=C}}$), 1201 (s), 863 (s). HRMS: calcd for $\text{C}_4\text{H}_3\text{N}^{80}\text{Se}$ 144.9431, found 144.943.

Selenocyanic Acid, Buta-2,3-diene Ester (13).²⁰ In a 250 mL flask were introduced, under nitrogen, potassium selenocyanate (2.88 g, 20 mmol) and acetonitrile (50 mL). 2,3-Butadien-1-ol, 4-methylbenzenesulfonate (4.48 g, 20 mmol) was slowly added, and the mixture was stirred for 6 h at room temperature. The mixture was then filtrated, the solvent was removed in vacuo, and the product was quickly distilled in vacuo and kept in a freezer ($-30\text{ }^{\circ}\text{C}$). Yield: 60%, bp $50\text{ }^{\circ}\text{C}$ (0.1 mbar). ^1H NMR (400 MHz, CDCl_3): δ 3.65 (td, $^3J_{\text{HH}} = 7.9\text{ Hz}$, $^5J_{\text{HH}} = 2.0\text{ Hz}$, 2H, CH_2); 4.99 (dt, $^4J_{\text{HH}} = 6.6\text{ Hz}$, $^5J_{\text{HH}} = 2.0\text{ Hz}$, 2H, C=CH₂); 5.42 (tt, $^3J_{\text{HH}} = 7.9\text{ Hz}$, $^4J_{\text{HH}} = 6.6\text{ Hz}$, 1H, C=CH). ^{13}C NMR (100 MHz, CDCl_3): δ 27.6 (t, $^1J_{\text{CH}} = 150.2\text{ Hz}$, $^1J_{\text{CSe}} = 49.0\text{ Hz}$ (d), CH_2); 77.8 (t, $^1J_{\text{CH}} = 169.4\text{ Hz}$, C=CH₂); 86.8 (d, $^1J_{\text{CH}} = 170.3\text{ Hz}$, C=CH); 101.5 (s, CN); 210.1 (s, C=C=C). ^{77}Se NMR (57.2 MHz, CDCl_3): δ 260.6. IR (film, cm^{-1}): 3060 (w, $\nu_{\text{C=CH}}$), 2989 (m), 2949 (m), 2151 (s, ν_{CN}), 1947 (s, $\nu_{\text{C=C}}$), 1195 (s), 858 (s), 639 (s). HRMS: calcd for $\text{C}_5\text{H}_5\text{N}^{80}\text{Se}$ 158.9587, found 158.958.

Selenocyanic Acid, Penta-3,4-diene Ester (14). In a 250 mL flask were introduced under nitrogen potassium selenocyanate (2.88 g, 20 mmol) and acetonitrile (50 mL). 3,4-Pentadien-1-ol, 4-methyl-

benzenesulfonate (4.76 g, 20 mmol) was slowly added, and the mixture was stirred for 3 h at $40\text{ }^{\circ}\text{C}$. The mixture was then filtrated, the solvent was removed in vacuo, and the product was distilled in vacuo. Yield: 80%, bp $63\text{ }^{\circ}\text{C}$ (0.1 mbar). ^1H NMR (400 MHz, CDCl_3): δ 2.61 (td, $^3J_{\text{HH}} = 7.0\text{ Hz}$, $^3J_{\text{HH}} = 6.6\text{ Hz}$, $^5J_{\text{HH}} = 3.0\text{ Hz}$, 2H, CH_2); 3.17 (t, $^3J_{\text{HH}} = 7.0\text{ Hz}$, 2H, CH_2), 4.83 (dt, $^4J_{\text{HH}} = 6.6\text{ Hz}$, $^5J_{\text{HH}} = 3.0\text{ Hz}$, 2H, C=CH₂); 5.20 (tt (quint), $^4J_{\text{HH}} = ^3J_{\text{HH}} = 6.6\text{ Hz}$, 1H, C=CH). ^{13}C NMR (100 MHz, CDCl_3): δ 28.4 (t, $^1J_{\text{CH}} = 147.0\text{ Hz}$, $^1J_{\text{CSe}} = 51.4\text{ Hz}$ (d), CH_2); 29.1 (t, $^1J_{\text{CH}} = 132.5\text{ Hz}$, CH_2); 77.2 (t, $^1J_{\text{CH}} = 167.9\text{ Hz}$, C=CH₂); 87.8 (d, $^1J_{\text{CH}} = 165.4\text{ Hz}$, C=CH); 101.7 (s, CN); 208.5 (s, C=C=C). ^{77}Se NMR (57.2 MHz, CDCl_3): δ 210.3. IR (film, cm^{-1}): 3059 (m, $\nu_{\text{C=CH}}$), 2987 (m), 2947 (m), 2150 (s, ν_{CN}), 1954 (s, $\nu_{\text{C=C}}$), 1435 (s), 1260 (s), 1200 (s), 851 (s). HRMS: calcd for $\text{C}_6\text{H}_7\text{N}^{80}\text{Se}$ 172.9744, found 172.972.

Synthesis of Propa-1,2-dieneselenol (9). 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 ($-30\text{ }^{\circ}\text{C}$), and aluminum chloride (1.0 g, 7.5 mmol) was added in portions. The reaction mixture was allowed to warm to $-10\text{ }^{\circ}\text{C}$ and stirred for 5 min. Compound **12** (432 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 $-10\text{ }^{\circ}\text{C}$. Succinic acid (4.72 g, 40 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, degassed, and then immersed in a cold bath ($-10\text{ }^{\circ}\text{C}$). 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 **9** was distilled off in vacuo (10^{-1} mbar) from the reaction mixture. The first trap cooled at $-50\text{ }^{\circ}\text{C}$ removed selectively the less volatile products, and compound **9** was condensed in the second trap equipped with two stopcocks and cooled at $-100\text{ }^{\circ}\text{C}$. At the end of the reaction, this second cell was disconnected from the vacuum line by stopcocks and adapted to the PE or mass spectrometer. On the other hand, to record the NMR spectra, this second trap was allowed to warm to room temperature and the products were condensed on a cold finger ($-196\text{ }^{\circ}\text{C}$) connected at the bottom to an NMR tube immersed in liquid nitrogen. A cosolvent (CDCl_3) was added at this step. After disconnection from the vacuum line by stopcocks, the apparatus was filled with dry nitrogen; liquid nitrogen was subsequently removed. The products were collected in the NMR tube and kept at low temperature ($<-50\text{ }^{\circ}\text{C}$) before analysis. Yield: 55%, bp $-55\text{ }^{\circ}\text{C}$ (0.1 mbar). $\tau_{1/2}$ (5% in CDCl_3 at room temperature): 15 h. ^1H NMR (400 MHz, CDCl_3): δ 0.85 (dt, $^3J_{\text{HH}} = 6.1\text{ Hz}$, $^5J_{\text{HH}} = 2.3\text{ Hz}$, $^1J_{\text{SeH}} = 50.2\text{ Hz}$ (d), 1H, SeH); 4.66 (dd, $^4J_{\text{HH}} = 6.1\text{ Hz}$, $^5J_{\text{HH}} = 2.3\text{ Hz}$, 2H, CH_2); 5.67 (td, $^4J_{\text{HH}} = ^3J_{\text{HH}} = 6.1\text{ Hz}$, 1H, CH–Se). ^{13}C NMR (100 MHz, CDCl_3): δ 67.8 (d, $^1J_{\text{CH}} = 191.1\text{ Hz}$, $^1J_{\text{CSe}} = 85.9\text{ Hz}$, CH); 77.0 (t, $^1J_{\text{CH}} = 169.5\text{ Hz}$, CH_2); 207.3 (s, C=C=C). ^{77}Se NMR (57.2 MHz, CDCl_3): δ 66.5. IR (gas phase, $20\text{ }^{\circ}\text{C}$, cm^{-1}): 2349.2 (s, ν_{SeH}), 1961.6 (m, $\nu_{\text{C=C}}$). HRMS: calcd for $\text{C}_3\text{H}_4^{80}\text{Se}$ 119.9478, found 119.947. The solvent-free sample prepared for photoelectron spectroscopy was fitted on the spectrometer and slowly allowed to warm to distill the product. However only a mixture of compounds was characterized in these conditions followed at the end by a quite good spectrum of 2-propyneselenol **3**.

Buta-2,3-dieneselenol (10) and Penta-3,4-dieneselenol (11). The procedure reported above for selenol **9** was used but without aluminum chloride. The temperature of traps takes into consideration the boiling point of products.

Buta-2,3-dieneselenol (10). First trap: $-30\text{ }^{\circ}\text{C}$. Second trap: $-90\text{ }^{\circ}\text{C}$. Yield: 50%, bp $-40\text{ }^{\circ}\text{C}$ (0.1 mbar). $\tau_{1/2}$ (5% in CDCl_3 at room temperature): 30 min. ^1H NMR (400 MHz, CDCl_3): δ -0.18 (t, $^3J_{\text{HH}} = 6.9\text{ Hz}$, $^1J_{\text{SeH}} = 45.3\text{ Hz}$, 1H, SeH); 3.21 (tdd, $^3J_{\text{HH}} =$

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7.9 Hz, $^3J_{\text{HH}} = 6.6$ Hz, $^5J_{\text{HH}} = 2.3$ Hz, 2H, CH₂); 4.86 (dt, $^4J_{\text{HH}} = 6.6$ Hz, $^5J_{\text{HH}} = 2.3$ Hz, 2H, C=CH₂); 5.39 ppm (tt, $^3J_{\text{HH}} = 7.9$ Hz, $^4J_{\text{HH}} = 6.6$ Hz, 1H, C=CH). ¹³C NMR (100 MHz, CDCl₃): δ 15.6 (t, $^1J_{\text{CH}} = 144.6$ Hz, $^1J_{\text{SeC}} = 46.6$ Hz (d), CH₂); 76.7 (t, $^1J_{\text{CH}} = 167.9$ Hz, C=CH₂); 91.3 (d, $^1J_{\text{CH}} = 167.0$ Hz, C=CH); 208.1 (s, C=C=C). ⁷⁷Se NMR (57.2 MHz, CDCl₃): δ 48.7. IR (film, 77 K, cm⁻¹): 3060 (w, $\nu_{\text{C}=\text{CH}}$), 3000 (m), 2939 (m), 2344 (s, $\nu_{\text{Se-H}}$), 1954 (m, $\nu_{\text{C}=\text{C}}$), 1454 (m). HRMS: calcd for C₄H₆⁸⁰Se 133.9635, found 133.964.

Penta-3,4-dieneselenol (11). First trap: -15 °C. Second trap: -70 °C. Yield: 82%, bp -25 °C (0.1 mbar). ¹H NMR (400 MHz, CDCl₃): δ -0.50 (t, $^3J_{\text{HH}} = 7.1$ Hz, $^1J_{\text{SeH}} = 47.3$ Hz, 1H, SeH); 2.43 (tdt, $^3J_{\text{HH}} = 6.9$ Hz, $^3J_{\text{HH}} = 6.6$ Hz, $^5J_{\text{HH}} = 3.3$ Hz, 2H, CH₂); 2.67 (dt, $^3J_{\text{HH}} = 7.1$ Hz, $^3J_{\text{HH}} = 6.9$ Hz, 2H, CH₂-Se), 4.75 (dt, $^4J_{\text{HH}} = 6.6$ Hz, $^5J_{\text{HH}} = 3.3$ Hz, 2H, C=CH₂); 5.14 (tt (quint), $^4J_{\text{HH}} = ^3J_{\text{HH}} = 6.6$ Hz, 1H, C=CH). ¹³C NMR (100 MHz, CDCl₃): δ 16.5 (t, $^1J_{\text{CH}} = 143.0$ Hz, $^1J_{\text{SeC}} = 49.0$ Hz (d), CH₂); 32.3 (t, $^1J_{\text{CH}}$

= 130.1 Hz, CH₂); 75.6 (t, $^1J_{\text{CH}} = 167.9$ Hz, C=CH₂); 88.8 (d, $^1J_{\text{CH}} = 163.0$ Hz, C=CH); 208.4 (s, C=C=C). ⁷⁷Se NMR (57.2 MHz, CDCl₃): δ -8.7. IR (film, 77 K, cm⁻¹): 3059 (m, $\nu_{\text{C}=\text{CH}}$), 2938 (m), 2342 (s, $\nu_{\text{Se-H}}$), 1956 (s, $\nu_{\text{C}=\text{C}}$), 1442 (m), 1124 (s), 849 (s). HRMS: calcd for C₅H₈⁸⁰Se 147.9791, found 147.978.

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Supporting Information Available: Tables 1S and 2S and ¹H and ¹³C NMR spectra of compounds **6**, **9–12**, and **14**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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