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Anna Chrostowska, Clovis Darrigan, Alain Dargelos, Alain Graciaa, Jean-Claude Guillemin. Isoselenocyanates versus Isothiocyanates and Isocyanates. *Journal of Physical Chemistry A*, 2018, 122 (11), pp.2894-2905. 10.1021/acs.jpca.7b12604 . hal-01744285

HAL Id: hal-01744285

<https://univ-rennes.hal.science/hal-01744285>

Submitted on 27 Apr 2018

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Isoselenocyanates *versus* Isothiocyanates and Isocyanates

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Dedicated to Professor Tamas Veszpremi for his 70th birthday.

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3
4 **Abstract.** Alkyl and aryl isoselenocyanates are well-known intermediates in the synthesis of
5 various organoselenium compounds but the knowledge of the physicochemical properties of
6 simple unsaturated derivatives is still fragmentary. Vinyl-, 2-propenyl- and cyclopropyl
7 isoselenocyanates have been prepared by reaction of selenium in powder with the
8 corresponding isocyanides. The isoselenocyanates of this series, with a variable distance
9 between the N=C=Se group and the unsaturated or pseudo-unsaturated group, have been
10 studied by UV-photoelectron spectroscopy and quantum chemical calculations. For each of
11 these three isoselenocyanates, the exploration of conformers and geometrical optimization
12 always converge toward only one local minimum. The vinyl and cyclopropyl derivatives are
13 characterized by similar order of magnitude of interactions between the NCSe group and the
14 substituent, while for allylic compound two non-interacting moieties should be considered.
15 The same conclusions were obtained for vinylic and cyclopropylic sulfur and oxygen
16 derivatives.
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18 Thus, the type and extent of interactions between the N=C=X (X = O, S, Se) group and an
19 unsaturated (vinyl, allyl or cyclopropyl) moiety are now clarified.
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1. Introduction.

Alkyl and aryl isoselenocyanates are very useful precursors or intermediates in the synthesis of biologically active organoselenium cyclic compounds or selenoureas.¹⁻⁵ However, the synthesis and the physicochemical properties of simple unsaturated isoselenocyanates have been little studied compared to those of alkylated derivatives. The synthesis of the simplest organoselenocyanate, $\text{CH}_3\text{-NCSe}$, was first reported in 1965,⁶ but so far only a few functionalized derivatives have been synthesized. As an exception, the unsubstituted allyl derivative, $\text{H}_2\text{C}=\text{CHCH}_2\text{NCSe}$, has been characterized as early as 1963,⁷ but in the presence of the allyl selenocyanate ($\text{H}_2\text{C}=\text{CHCH}_2\text{SeCN}$) due to a [3,3]-sigmatropic rearrangement between both forms. In a study on such rearrangements with selenium derivatives, Banert and Toth⁸ reported a pioneering work on the formation of the simplest allenyl isoselenocyanate and substituted allenyl and vinyl derivatives. Recently the first preparation of the simplest vinyl isoselenocyanate ($\text{H}_2\text{C}=\text{CHNCSe}$) was reported and its microwave spectrum was recorded.⁹

The use of UV-photoelectron spectroscopy assisted by theoretical calculations in quite recent studies on unsaturated isocyanides,¹⁰ selenols, selenocyanides,^{11,12} and tellurols,¹³ has clarified the nature of the interactions between the heteroatomic group and the unsaturated substituent depending on the distance between the two functional groups. This approach was particularly well adapted to reveal similarities and differences in the orbitals more or less perturbed by the nature of interactions between groups. To the best of our knowledge, in the case of isoselenocyanates, only the photoelectron spectra of alkylated and silylated derivatives have been reported.¹⁴⁻¹⁶ For α,β - or β,γ -unsaturated isoselenocyanates, interactions between NCSe and unsaturated groups can be identified and compared with those of a compound having a pseudo-unsaturated substituent such as cyclopropyl isoselenocyanate, with reported data on saturated isoselenocyanates and those of the isoelectronic oxygen or sulfur derivatives. We report here the photoelectron spectra of vinyl-, allyl- and cyclopropyl-isoselenocyanates **1-3** followed by the comparison of these spectra with those of the corresponding oxygen **4-6** and sulfur derivatives **7-9** analyzed for this study (Chart 1). The result of this study sheds some light to the understanding of the differences or similarities between unsaturated isocyanates, isothiocyanates and isoselenocyanates.

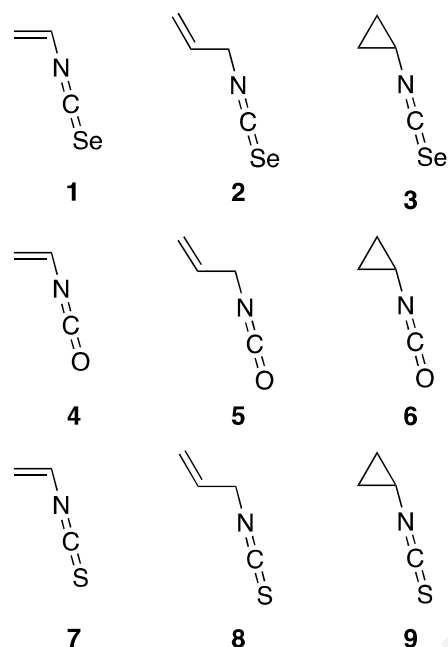


Chart 1. Vinyl-, allyl- and cyclopropyl-isoselenocyanates **1-3**; vinyl-, allyl- and cyclopropyl-isocyanates **4-6**; vinyl-, allyl- and cyclopropyl-isothiocyanates **7-9**.

Experimental Section

Materials.

Allyl isocyanate **5** and allyl isothiocyanate **8** were purchased from the Aldrich Company. Vinyl isoselenocyanate **1**⁹, cyclopropyl isocyanate **4** and vinyl isothiocyanate **7**¹⁷ have been synthesized as reported.

Caution: Isoselenocyanates are foul-smelling liquids and potentially toxic species that should be prepared under a well-ventilated hood.

*Synthesis of allyl **2** and cyclopropyl isoselenocyanate **3**.* Into a one-necked cell equipped with a stopcock were introduced under nitrogen the isocyanide (670 mg, 10 mmol), chloroform (10 mL), selenium powder (950 mg, 12 mmol), and few drops of tri-*n*-octylamine. The mixture was immersed in a liquid nitrogen bath and degassed. The stopcock was closed, and the mixture was heated at 50 °C (**2**) or 65 °C (**3**) overnight. The cell was then adapted to a vacuum line equipped with a U-tube with stopcocks and immersed in a bath cooled at -45 °C. The solution was heated to 60 °C and distilled *in vacuo* (0.1 mbar). The isoselenocyanate **2,3**

was selectively trapped at $-45\text{ }^{\circ}\text{C}$. A second distillation can be performed to obtain a very pure sample.

Allyl isoselenocyanate 2.^{7,8} Yield: 37 %, 540 mg. $\text{bp}_{0.1\text{mbar}} \approx 60\text{ }^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 400 MHz) δ 4.18 (dt, 1H, $^3\text{J}_{\text{HH}} = 4.9\text{ Hz}$, $^4\text{J}_{\text{HH}} = 1.8\text{ Hz}$, $\text{CH}_2\text{-N}$), 5.32 (dt, 1H, $^3\text{J}_{\text{HHtrans}} = 15.0\text{ Hz}$, $^4\text{J}_{\text{HH}} = 1.8\text{ Hz}$, $\text{HCH}=\text{C}$), 5.41 (dt, 1H, $^3\text{J}_{\text{HHcis}} = 10.1\text{ Hz}$, $^4\text{J}_{\text{HH}} = 1.8\text{ Hz}$, $\text{HCH}=\text{C}$), 5.82 (ddt, 1H, $^3\text{J}_{\text{HHtrans}} = 15.0\text{ Hz}$, $^3\text{J}_{\text{HHcis}} = 10.1\text{ Hz}$, $^3\text{J}_{\text{HH}} = 4.9\text{ Hz}$, CH). ^{13}C NMR (CDCl_3 , 100 MHz) δ 47.5 (t, $^1\text{J}_{\text{CH}} = 155.3\text{ Hz}$, CH_2), 118.5 (t, $^1\text{J}_{\text{CH}} = 158.4\text{ Hz}$, $\text{CH}_2=\text{C}$), 124.8 (s, NCSe), 129.1 (d, $^1\text{J}_{\text{CH}} = 160.6\text{ Hz}$, $\text{CH}_2=\text{CH}$). A few percent of two minor impurities were observed in the PE and NMR spectra, the allyl selenocyanide coming from a [3,3]-sigmatropic rearrangement^{7,8} and the allyl isocyanide coming from the departure of the selenium atom.

Cyclopropyl isoselenocyanate 3. Yield: 47 %, 686 mg. $\text{bp}_{0.1\text{mbar}} \approx 60\text{ }^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 400 MHz) δ 0.89 (m, 2H, c- CH_2), 0.99 (m, 2H, c- CH_2), 2.93 (dddd, 1H, $^3\text{J}_{\text{HH}} = ^3\text{J}_{\text{HH}} = 7.3\text{ Hz}$, $^3\text{J}_{\text{HH}} = ^3\text{J}_{\text{HH}} = 3.7\text{ Hz}$, CH). ^{13}C NMR (CDCl_3 , 100 MHz) δ 8.46 (t, $^1\text{J}_{\text{CH}} = 166.6\text{ Hz}$, c- CH_2), 25.5 (d brd, $^1\text{J}_{\text{CH}} = 190.7\text{ Hz}$, CH), 118.4 (s brd, NCSe). HRMS calcd for $\text{C}_4\text{H}_5\text{N}^{80}\text{Se}^+$: 146.9587. Found: 146.959. IR [ν (cm^{-1}), gas phase] 3091 (w, ν_{CH_2}), 3010 (m, ν_{CH_2}), 2924 (m), 2853 (w), 2142 (s, ν_{NCSe}), 1349 (s), 1031 (m), 964 (m), 812 (m).

Computational Methods.

All calculations were performed using the Gaussian 09¹⁸ software with the 6-311G(d,p) basis set. DFT has been shown to predict various molecular properties of similar compounds successfully.¹⁹ All geometry optimizations were carried out with the range-separated hybrid CAM-B3LYP²⁰⁻²³ functional. Frequency calculations were performed in order to verify that the stationary points obtained were true energy minima. Possible conformers were investigated and optimized to find the most stable one. First vertical ionization energy ($IE_{1,\nu}$) was calculated with $\Delta\text{SCF-DFT}$, as a difference between ground states of cation and neutral ($IE_{1,\nu} = E^{\text{cation}} - E^{\text{neutral}}$) at the same geometry (of neutral system).²⁴⁻²⁶ The TDDFT²⁷⁻³⁰ approach was used for the calculation of higher ionization energies in combination with $\Delta\text{SCF-DFT}$ method.^{29,31,32} The vertical ionization energies were also calculated at the *ab initio* level according to OVGf^{33,34} and SAC-CI³⁵⁻³⁷ (Symmetry Adapted Cluster/Configuration Interaction) methods. We also use Koopmans' theorem³⁸ for a rough estimation of IE, within frozen orbital approximation ($IE_1 = -\epsilon_{\text{HOMO}}^{\text{KS}}$). Natural bonding analysis^{39,40} was performed with package included in Gaussian. Avogadro software^{41,42} has been used as a visualization tool for MOs.

Photoelectron Spectroscopy.

The UV-PES spectra were recorded on a home-built (at the Institut of “Sciences Analytiques et de Physico-Chimie pour l’Environnement et les Matériaux” (IPREM)) three-part spectrometer equipped with a main body device, He-I radiation source (21,21 eV and/or 48 eV) and a 127° cylindrical analyzer. The spectrometer works at constant analyzer energy under $5 \cdot 10^{-6}$ Torr working pressure and $\leq 10^{-7}$ Torr for channeltron (X914L) pressure. The monitoring is done by a microcomputer supplemented by a digital–analogue converter (AEI spectrum). The spectra resulting from a single scan are built from 2048 points and are accurate within 0.05 eV. Spectra are calibrated with lines of xenon (12.13 and 13.44 eV) and of argon (15.76 and 15.94 eV). The accuracy of the ionization potentials is + 0.03 eV for sharp peaks and ± 0.05 eV for broad and overlapping signals.

Compounds **1-3** and **5-8** were slowly vaporized under low pressure (10^{-6} Torr) inside handmade three valves injector (3/4 inch diameter; 10 cm length; working temperature: $-190 \text{ }^\circ\text{C} \leq T \leq +300 \text{ }^\circ\text{C}$) and the gaseous flow was then continuously and simultaneously analyzed by UV-photoelectron spectrometry.

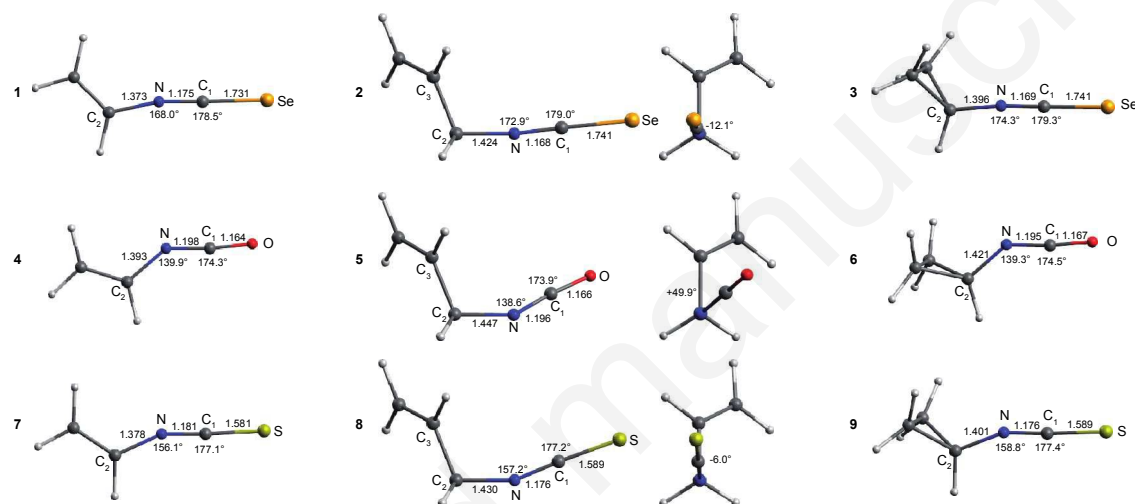
2. Results and Discussion

Calculated geometrical structures

To the best of our knowledge, conformational analyses on allyl isoselenocyanate **2** or cyclopropyl isoselenocyanate **3** have not been investigated until now. In the allylic series, the presence of two conformers in the gas phase was predicted for allyl isocyanate **5**⁴³ and allyl isothiocyanate **8**,⁴⁴ but only one conformer was characterized for each of them by microwave spectroscopy.^{45,46} Microwave spectra of both conformers were recorded for cyclopropyl isocyanate **6**^{47,48} and cyclopropyl isothiocyanate **9**,^{49,50} the antiperiplanar conformer being more abundant in both cases in the gas phase. For vinylic derivatives, theoretical calculations concluded that for any $\text{H}_2\text{C}=\text{CHNCX}$ ($X = \text{O}, \text{S}, \text{or Se}$) both CCNC synperiplanar (**sp**) and antiperiplanar (**ap**) conformers should be present in the gas phase.⁵¹ However, even if both conformers were observed by microwave spectroscopy for $\text{H}_2\text{C}=\text{CHNCO}$ **4** with a major **ap** conformer,⁵² only the **ap** form was characterized for the sulfur⁵³ and selenium derivative.⁹ In this recent study on vinyl isoselenocyanate **1**, among the five different quantum chemical methodologies employed, namely MP2, CCSD(T), CCSD, B3LYP and M062X, only MP2

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2 predicted the existence of a synperiplanar form, which has not been found in the microwave
3 spectra.

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6 In order to elucidate the electronic structure differences of the three isoselenocyanates under
7 study, CAM-B3LYP functional and 6-311G(d,p) basis set were applied to calculate
8 geometrical structures of molecules **1-3**. The selected geometrical parameters of most stable
9 conformers (see Computational Methods for more details) of vinyl, allyl and cyclopropyl
10 derivatives **1-9** are shown in Figure 1.



34 **Figure 1.** Selected geometrical parameters of: vinyl isoselenocyanate **1**, allyl
35 isoselenocyanate **2**, cyclopropyl isoselenocyanate **3**, vinyl isocyanate **4**, allyl isocyanate **5**,
36 cyclopropyl isocyanate **6**, vinyl isothiocyanate **7**, allyl isothiocyanate **8** and cyclopropyl
37 isothiocyanate **9**. Bond lengths are in angstrom, angles in degree. For **2**, **5** and **8**, the views in
38 alignment of C₂-N bond allow to show the variation in dihedral angles C₁-N-C₂-C₃.

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45 For each isoselenocyanate **1-3**, the geometrical optimization and conformational analysis
46 always converge toward a unique local minimum (Figure 1). For vinyl isocyanate **4** and
47 cyclopropyl isocyanate **6**, two conformers (local minima) were found, corresponding to
48 antiperiplanar and synperiplanar forms (C_s symmetry). In both cases, the most stable
49 conformer is **ap**, as shown in Figure 1 (see Supporting Information for details). The
50 conformational analysis and geometrical optimization of allylisocyanate **5** and isothiocyanates
51 **7-9** converge for each compound toward a unique local minimum as already observed for
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2 isoselenocyanates **1-3** (Figure 1). Despite that cyclopropyl isothiocyanate **9** has been
3 described under different conformers,⁴⁹ CAM-B3LYP functional only converges to **ap**
4 geometry. Results with B3LYP are slightly different since we found both **ap** and **sp** forms,
5 very close in energy (**ap** being the most stable). For R = vinyl, allyl or cyclopropyl in the R-
6 NCX series, we noted the same tendency of shortening C₂-N and N-C₁ bonds, and
7 enlargement of the bond angle C₂NC₁ in the order O, S, Se. Nitrogen center changes from
8 bent “*sp*²” hybridization in NCO to quasi-linear “*sp*” hybridization in NCSe. For the RNCO
9 series, the C₂-N bond length is bigger when C₂NC₁ bond angle is smaller in order: **4**, **6**, **5**. In
10 all cases, NCX is not linear; the smallest values for NCX angle correspond to the NCO (**5**:
11 173.9°; **4**: 174.3°; **6**: 174.5°), but the nearly linear framework is calculated for NCSe group (**1**:
12 178.5°; **2**: 179.0°; **3**: 179.3°). The most remarkable parameter change is the dihedral angle
13 variation between allyl and NCX groups (C₁-N-C₂-C₃ torsion angle): very different from a
14 synperiplanar conformation for NCO group (+49.9°), but close to a synperiplanar
15 conformation for NCS and NCSe groups (-6° and -12.1°, respectively). The bond length
16 between C₁ and heteroatom X is increasing, with respect to atomic radius of X.
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27 The Natural Bonding Orbital (NBO) analysis of these compounds (Figure 2) gives more
28 precise information related to geometrical description. In the case of NCSe and NCS groups,
29 the N-C₁ bond looks like a triple bond (occupation close to 6 electrons), whereas C₁-S and C₁-
30 Se bonds correspond clearly to a single bond (occupation close to 2 electrons). Nitrogen has
31 no more its lone pair in these cases; these configurations correspond to R-N≡C-X Lewis'
32 structure. For the NCO group, NBO's occupations clearly indicate that N-C₁ bond should be
33 considered as a double bond (occupation close to 4 electrons) as well as the C₁-O bond, with a
34 true lone pair localized on nitrogen. Such compounds correspond to R-N=C=O Lewis'
35 structure. These NBO results are consistent with previous geometrical description: for NCO
36 series, C₁NC₂ bond angle increases while hybridization parameter λ decreases (allyl:
37 138.6°/*sp*^{1.59}; cyclopropyl: 139.3°/*sp*^{1.51}; vinyl: 139.9°/*sp*^{1.42}). For NCS and NCSe series, this
38 trend cannot be confirmed, due to a very low variation of parameter λ (near 1.11±0.01).
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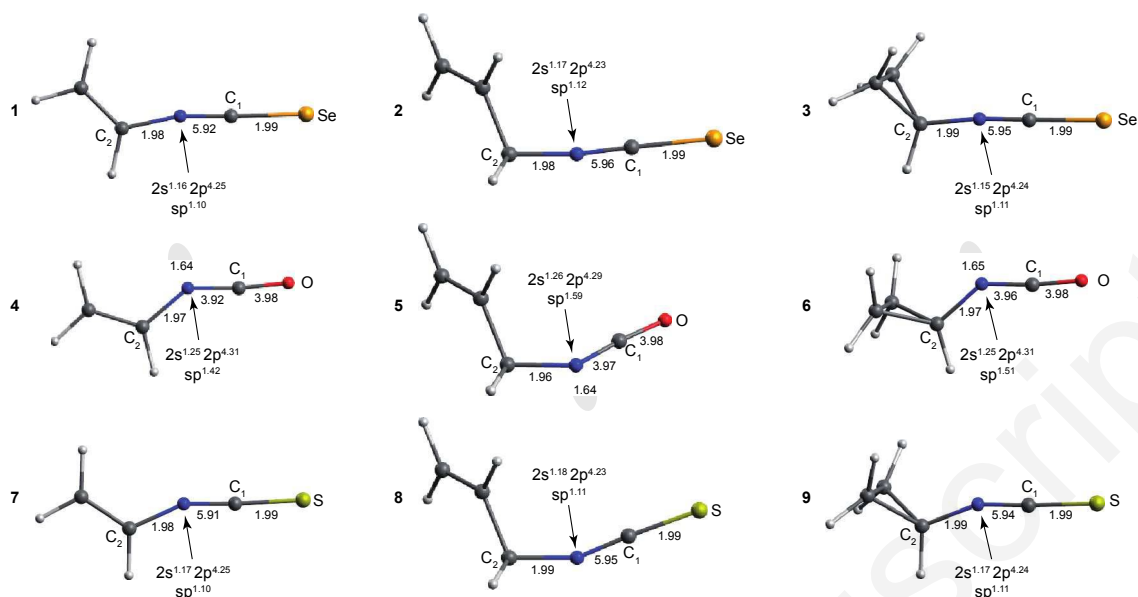


Figure 2. Natural Bonding Orbital (NBO) analysis of compounds **1-9**. Numbers on bonds correspond to NBO's occupations (single bond close to 2; double bond close to 4; triple bond close to 6; lone pair of nitrogen represented in grey). Natural electron configuration ($2s^m 2p^n$) for nitrogen atom is given, and also sp^{λ} hybridization of nitrogen in C₂-N bond.

Synthesis of Isoselenocyanates 1-3.

Vinyl **1**, allyl **2** and cyclopropyl isoselenocyanate **3** have been synthesized by heating of a mixture of the corresponding isocyanide with selenium in the presence of a base, the tri-n-octylamine, and with chloroform as solvent. Purification was performed on a vacuum line by selective trapping of the isoselenocyanates. Characterization was performed by ¹H and ¹³C NMR spectroscopy and high-resolution mass spectrometry. In ¹³C NMR spectroscopy, the broad signal around δ 125 ppm is typical of the NCSe chemical shift.

UV-photoelectron spectra assignments and theoretical evaluation of ionization energies

The photoelectron spectra of the vinyl isocyanate **4**⁵² and cyclopropyl isothiocyanate **9**⁵⁴ have already been recorded and analyzed. However, for sake of consistency and to allow a direct comparison between the compounds under current investigation, we also calculated the IEs of previously published UV-PES results of compounds **4**⁵² and **9**.⁵⁴ For the reliable

assignment of PE bands, density functional theory [Δ SCF+TD-DFT (CAM-B3LYP)] and *ab initio* (OVGF and SAC-CI) calculations of ionization energies using the 6-311G(d,p) basis set have been carried out on optimized geometrical structures of **1-9**. The comparison of the theoretically predicted IEs and experimental data are summarized in Tables 1-3 and S1-S6 in the Supp. Inf. section.

The recorded UV-photoelectron spectra of vinyl isoselenocyanate **1** and vinyl isothiocyanate **7** are depicted in Figure 3. The PE spectrum of isoselenocyanate **1** shows two first IEs at 8.9 eV and 10.8 eV, which are followed by a group of three broad bands at 12.8, 13.9 and 14.65 eV. The first intense PE band of isothiocyanate **7** is located at 9.1 eV and is well separated from the less intense, right side shoulder at 9.6 eV. The sharp band at 11.1 eV is followed by higher-energy ionizations at 12.9 and 13.85 eV.

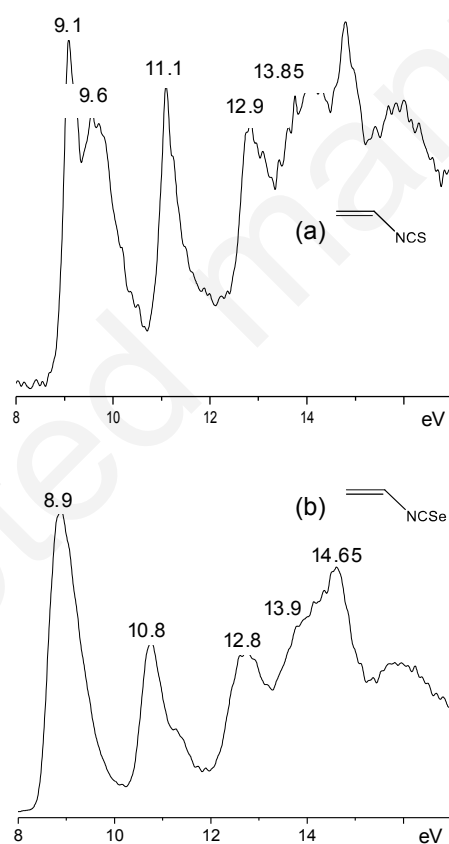


Figure 3. UV-Photoelectron spectra of (a) vinyl isothiocyanate **7**; (b) vinyl isoselenocyanate **1**.

The assignment of these experimental results is corroborated by the theoretical evaluation of ionization energies and is summarized in Table 1 for vinyl isoselenocyanate **1**, and in Table 3 for vinyl isothiocyanate **7**, while Table 2 contains previously published UV-

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2 PES data of vinyl isocyanate **4**.⁵² Also, the comparison of all UV-PES data of studied
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4 compounds **1**, **4**, **7** with those of methyl isocyanate, isothiocyanate and isoselenocyanate, as
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6 well as of the parent acids HNCO and HNCS, is useful. After some debate, the assignment of
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8 UV-PES data of these compounds have been clarified using Penning ionization electron
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10 spectroscopy.^{55,56} The experimentally determined first IEs for CH₃NCX series (X = O: 10.67
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12 eV; X = S: 9.35 eV; X = Se: 8.93 eV)¹⁴ show clearly the significant influence of the
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14 chalcogen atom on the energetic position of the corresponding HOMO. For these three alkyl
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16 derivatives,¹⁴ the first and second ionization energies correspond to the out-of-phase (π^* and π
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18 \perp^*) MOs of the -NCX (X = O, S, Se) group. For the vinyl substituted RNCX series, the first
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20 IEs of **1**, **4** and **7** arise from the antibonding interaction between the π^*_{NCX} and the $\pi_{\text{C=C}}$ MOs
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22 of vinyl substituent, while the third IEs are linked with the antibonding interaction between
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24 the π_{NCX} and the $\pi_{\text{C=C}}$ MOs. The contribution of the p orbital of sulfur and selenium,
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26 respectively, is quite important, and these interactions lower the first IE value in comparison
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28 with their oxygen analogue: IE = 9.8 eV for **4**,⁵² 9.1 eV for **7** and 8.9 eV for **1**. For the third
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30 IEs, this destabilizing effect is even more pronounced and follows to the lower IE values
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32 versus CH₂=CH-NCO (12.65 eV) by 1.55 eV for **7** (11.1 eV) and by 1.85 eV for **1** (10.8 eV).
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34 It should be stressed that the nature of the first IE of **1**, **4** and **7** is substantially the same, but in
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36 the case of the third IE, the bonding interaction between the vinyl group and the nitrogen lone
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38 pair is privileged in **4**, while the bonding interaction between nitrogen lone pair and π_{CSe}
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40 is noted in **1**.

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42 The second IEs of **1**, **4** and **7** are attributed to the π^*_{NCX} in interaction with the σ_{CH}
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44 (8.9 eV for **1**; 11.28 eV for **4**; 9.6 eV for **7**), while the nature of the fourth, also of a'
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46 symmetry, corresponds to the π^*_{NCX} in interaction with the σ_{CH} in the case of **1** (12.8 eV) and
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48 **7** (12.9 eV), but to the fifth IE for **4** (14.97 eV); the fourth band of **4** (14.03 eV) is attributed
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50 to the σ^-_{CH} ionization.

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52 The comparison of these data for the first four IE values is presented on Figure 4.
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Table 1. Comparison of calculated and experimental ionization energies [eV] of vinyl isoselenocyanate **1**.

MO's nature		CAM-B3LYP $-\varepsilon_{KS}^{KS}$	CAM-B3LYP Δ SCF+TD-DFT	OVGF	SAC-CI	Exp.
a'' $\pi^*_{NCSe} - \pi_{CC}$		7.751	8.621	8.329	8.825	8.9
a' $\pi^*_{\perp NCSe}$		8.010	8.920	8.497	8.522	8.9
a'' $\pi_{CC} - \pi_{NCSe}$		10.211	11.007	10.871	10.976	10.8
a' $\pi^*_{\perp NCSe} - \sigma_{CH}$		12.532	12.991	12.995	13.064	12.8
a' $\sigma_{CH}; n^{\sigma}_{Se}$		13.243	13.356	13.914	14.074	13.9
a' $n^{\sigma}_{Se}; \sigma_{CH}$		13.611	13.967	14.606	14.668	14.65

Table 2. Comparison of calculated and experimental⁵² ionization energies [eV] of vinyl isocyanate 4.

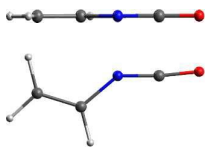
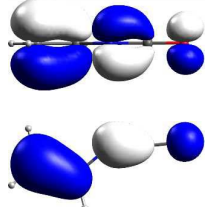
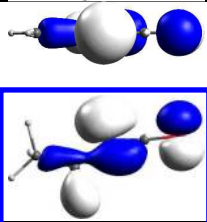
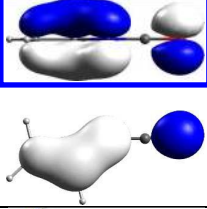
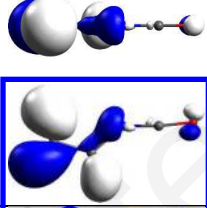
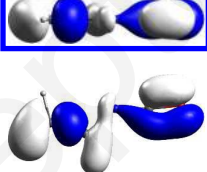
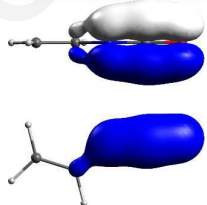

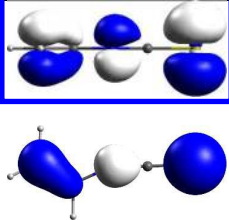
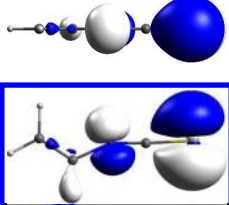
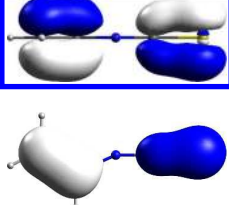
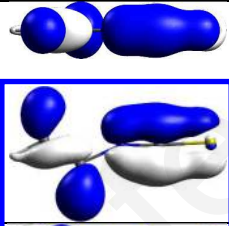
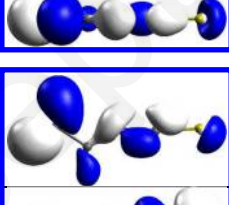
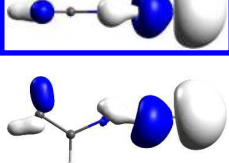
MO's nature		CAM-B3LYP $-\epsilon_{KS}$	CAM-B3LYP Δ SCF+TD- DFT	OVSF	SAC-CI	Exp.
a'' $\pi^*_{NCO} - \pi_{CC}$		8.511	9.543	9.468	9.405	9.8
a' $\pi^*_{\perp NCO}$		10.199	11.277	10.992	11.087	11.28
a'' $\pi_{CC} + \pi^*_{NCO}$		11.699	12.816	12.563	12.640	12.65
a' σ_{CH}		12.868	13.866	14.186	14.150	14.03
a' $\pi^*_{\perp NCO} - \sigma_{CH}$		13.992	15.064	15.079	15.079	14.97
a'' π_{NCO}		15.023	15.708	15.897	15.854	15.43

Table 3. Comparison of calculated and experimental ionization energies [eV] of vinyl isothiocyanate 7.

MO's nature		CAM-B3LYP $-\epsilon^{KS}$	CAM-B3LYP Δ SCF+TD- DFT	OVGF	SAC-CI	Exp.
a'' $\pi^*_{NCS} - \pi_{CC}$		8.113	8.961	8.594	8.667	9.1
a' $\pi^*_{\perp NCS}$		8.670	9.599	9.060	9.117	9.6
a'' $\pi_{CC} - \pi_{NCS}$		10.440	11.343	11.032	11.127	11.1
a' $\pi^*_{\perp NCS} - \sigma_{CH}$		12.614	13.275	13.129	13.145	12.9
a' σ_{CH}		13.272	14.114	14.259	14.306	13.85
a' $n^*_{S}; \sigma_{CH}$		13.970	15.038	14.666	14.815	14.1

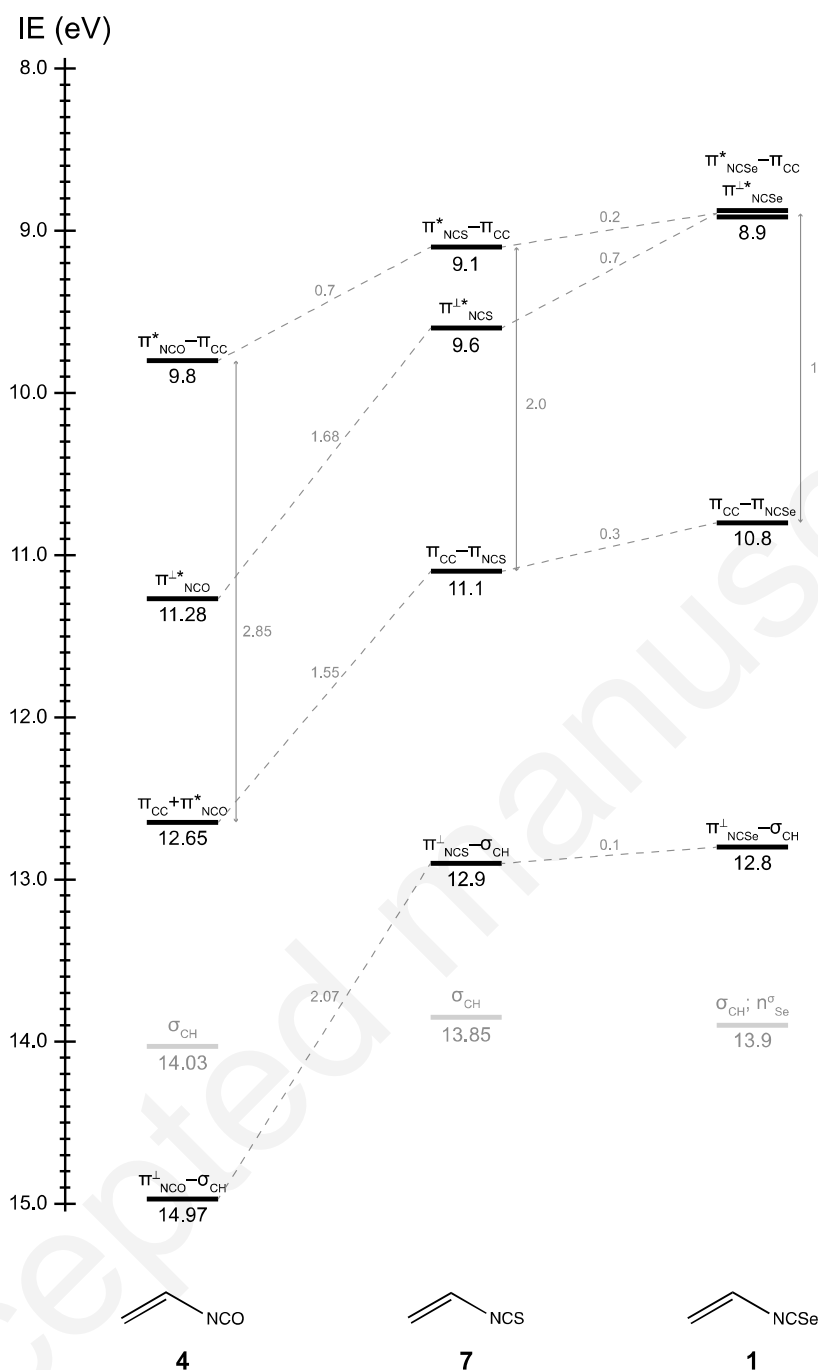


Figure 4. Comparison of the first four experimental ionization energies [eV] of vinyl isocyanate **4**,⁵² vinyl isothiocyanate **7** and vinyl isoselenocyanate **1**.

The influence of the chalcogen atom in the series of vinyl isocyanates -N=C=X (X = O, S, Se) is clearly evidenced by the global lowering of all IEs with sulfur or selenium containing -N=C=X functional group in comparison with -N=C=O. The HOMO energy increases (IE decreases) by 0.7 eV for vinyl isothiocyanate and by 0.9 eV for vinyl

isosenocyanate in comparison with the vinyl isocyanate, respectively. It should be noted that the next MO energies destabilizations are really significant if going from X = O to X = S or X = Se, as for example for the 2nd IEs: 1.68 eV for X = O → X = S and 2.38 eV for X = S → X = Se. The energy difference between the first and the third IEs corresponds to the strength of vinyl substituent ($\pi_{C=C}$) interaction with -N=C=X group and is the biggest one for CH₂=CH-NCO (2.85 eV), while for CH₂=CH-NCS (2.0 eV) and CH₂=CH-NCSe (1.9 eV) this difference is significantly weaker.

It should be stressed that the theoretical evaluation of ionization energies (IEs) fits very nicely with the Time-Dependent Density Functional Theory (TD-DFT) method, combined with Δ SCF approach (Δ SCF+TD-DFT), while outer valence green function (OVGF) and SAC-CI *ab initio* methods slightly underestimate two first IEs in the case of isosenocyanate **1** and isothiocyanate **7**, versus experimental data, respectively.

Figure 5 displays the UV-PE spectra of allyl isosenocyanate **2**, allyl isocyanate **5** and allyl isothiocyanate **8**. The comparison of these experimental data with Δ SCF/TD-DFT, OVGF and SAC-CI calculated IEs is presented in Tables S1 (for **2**), S3 (for **5**) and S5 (for **8**) in the Supporting Information. For the allyl isosenocyanate **2** (the impurity at 8.2 eV corresponds probably to Se₂ or polymeric selenium^{57,58}) and allyl isothiocyanate **8**, the two first IEs (**2**: 8.75 eV) (**8**: 9.25 eV) are due to the nearly isolated -NCX ionizations (π^*_{NCX} and $\pi^{\perp*}_{NCX}$). The almost non-perturbed $\pi_{C=C}$ ionization appears as the second band in the case of **2** (10.5 eV) and **8** (10.55 eV) and at the same value as for ethylene (10.55 eV).⁵⁹ The third, fourth and fifth bands of **2** and **8** are attributed to the $\pi^{\perp}_{NCX} - \sigma_{CH}$, $\pi_{NCX} - \sigma_{CH}$, $\pi^{\perp}_{NCX} - \sigma_{CC}$ MO's ionizations, respectively. The situation is quite different for allyl isocyanate **5**: the first PE band (located at 10.25 eV) corresponds to the through-space antibonding interaction between the π^*_{NCO} and the $\pi_{C=C}$ MOs of allyl substituent, while the second IE is linked with the through-space antibonding interaction between the $\pi^{\perp*}_{NCO}$ and the π . . . MOs (**5** 10.7 eV). The third PE band of **5** is associated with the $\pi^{\perp*}_{NCO}$ and the $\sigma_{.H}$ MOs (11.1 eV) and the fourth one (13.0 eV) to the pseudo- π of CH₂.

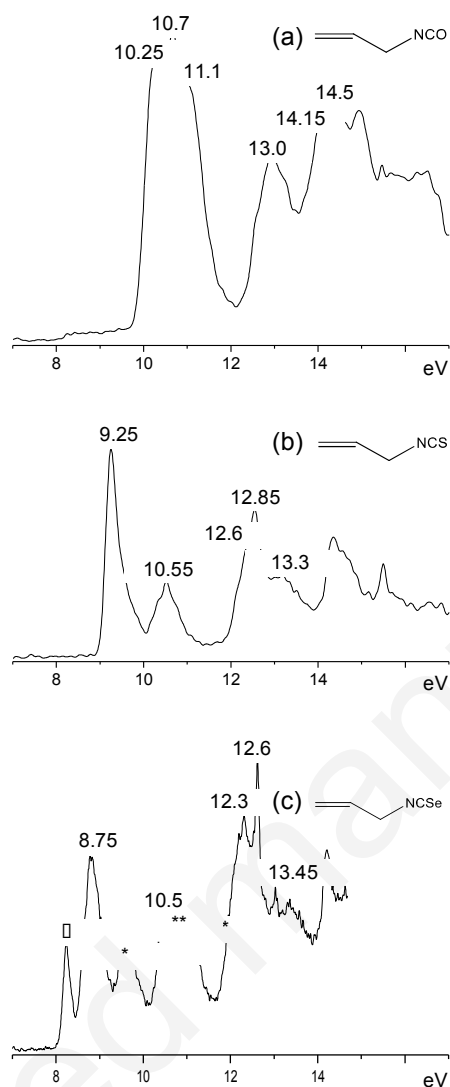


Figure 5. UV-Photoelectron spectra of (a) allyl isocyanate **5**; (b) allyl isothiocyanate **8**; (c) allyl isoselenocyanate **2**, \diamond impurity, * allyl-selenocyanate, ** allylisocyanide (see Experimental Section).

The influence of the chalcogen atom in the allyl substituent series is illustrated by the comparison of the first four experimental ionization energies of allyl isocyanate **5**, allyl isothiocyanate **8** and allyl isoselenocyanate **2** (Figure 6). As noted for vinyl derivatives, the replacement of the oxygen atom by sulfur causes a destabilization of HOMO (1 eV), while for selenium this destabilization is more important (1.5 eV). The same tendency, but of greater impact is observed with allyl derivatives for HOMO-1 ($X = O \rightarrow X = S$ 1.45 eV; $X = O \rightarrow X = Se$ 1.95 eV). The most important difference concerns the isocyanate unit interacting through space with allyl substituent, whereas it does not take place for isothiocyanate **8** and isoselenocyanate **2**. Keeping with this, we can consider rather two isolated moieties in the case of the $H_2C=CH-CH_2-NCS$ and $H_2C=CH-CH_2-NCSe$ molecules.

The comparison between vinyl isocyanate and allyl isocyanate shows much weaker interaction between allyl (0.85 eV) than vinyl (2.85 eV) and -NCO functional group.

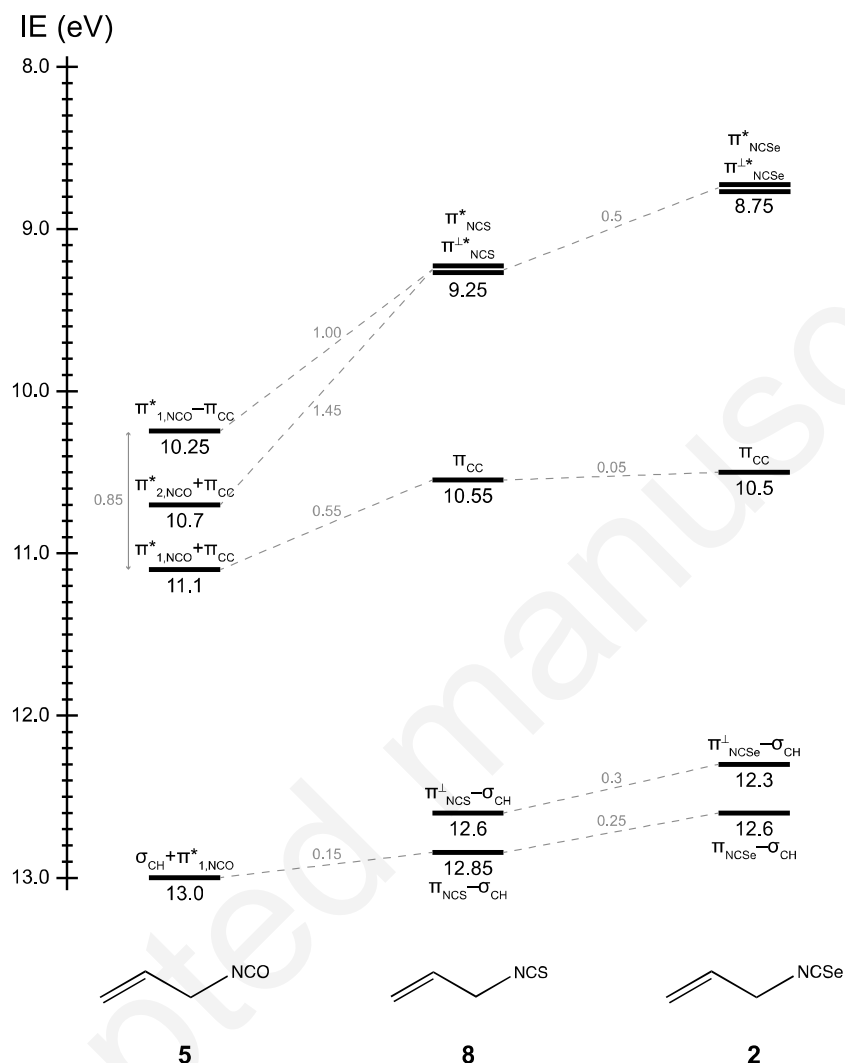


Figure 6. Comparison of the first four experimental ionization energies [eV] of allyl isocyanate **5**, allyl isothiocyanate **8** and allyl isoselenocyanate **2**.

To study cyclopropyl derivatives, a new compound, the cyclopropyl isoselenocyanate **3**, has been synthesized. For cyclopropyl isothiocyanate **9**,⁵⁴ it has been reported that the interaction of Walsh orbitals ω_S and ω_A of the cyclopropyl ring with the two out-of-plane combinations of π_2 of the isothiocyanato group (IE = 9.09 eV: $\pi_2(NCS) - \omega_A$; IE = 9.45 eV: $\pi_2(NCS) - \omega_S$) lowers the first and second IEs of the corresponding methyl isothiocyanate by 0.26 and 0.15 eV, respectively. The UV-photoelectron spectra of cyclopropyl isoselenocyanate **3** and

cyclopropyl isocyanate **6** are shown in Figure 7, and the corresponding IE calculations in comparison with experimental data are given in Tables S2 and S4. For the consistency of comparison, the known PE spectrum of cyclopropyl isothiocyanate **9**⁵⁴ and its interpretation are reported in Table S6. The low-energy band of cyclopropyl isoselenocyanate **3** at 8.45 eV (a'') arises from the ionization of the π^*_{NCSe} orbital in antibonding interaction with the Walsh orbital ω_A , while the second band at 8.6 eV, (a') is assigned mainly to the $\pi^{\perp*}_{\text{NCSe}}$. The $\omega_A - \pi^*_{\text{NCSe}}$ (a'') and $\omega_S - \pi^{\perp*}_{\text{NCSe}}$ (a') MO's ionizations appear at 10.95 eV and 11.4 eV, respectively. The first IE of cyclopropyl isocyanate **6** (9.9 eV, a'') arises from the removal of an electron from the π^*_{NCO} in antibonding interaction with the Walsh⁶⁰ orbital ω_A , while the second IE (10.75 eV, a') is assigned to the $\pi^{\perp*}_{\text{NCO}}$ in antibonding interaction with the Walsh orbital ω_S . The next two ionizations (12.3 eV, a'; 12.7 eV, a'') correspond to the $\omega_S - \pi^{\perp*}_{\text{NCO}}$ and $\omega_A - \pi^*_{\text{NCO}}$, respectively. Higher energy ionizations are due to the $\sigma_{\text{C-H}}$, $\sigma_{\text{C-C}}$ and bonding combinations of π NCO moiety with Walsh orbitals. As for cyclopropyl isoselenocyanate **3**, higher energy ionizations are due to the $\sigma_{\text{C-H}}$, $\sigma_{\text{C-C}}$ and bonding combinations of π NCO moiety with Walsh orbitals.

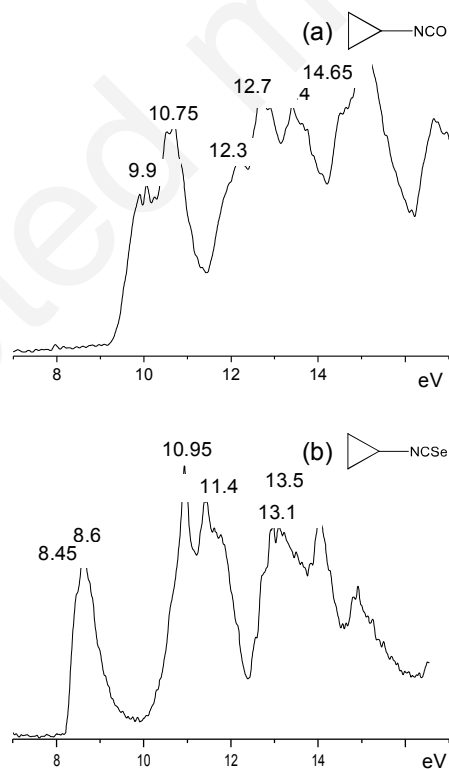


Figure 7. UV-Photoelectron spectra of (a) cyclopropyl isocyanate **6**; (b) cyclopropyl isoselenocyanate **3**.

Figure 8 summarizes the first four experimental ionization energies of cyclopropyl isocyanate **6**, cyclopropyl isothiocyanate **9**⁵⁴ and cyclopropyl isoselenocyanate **3**.

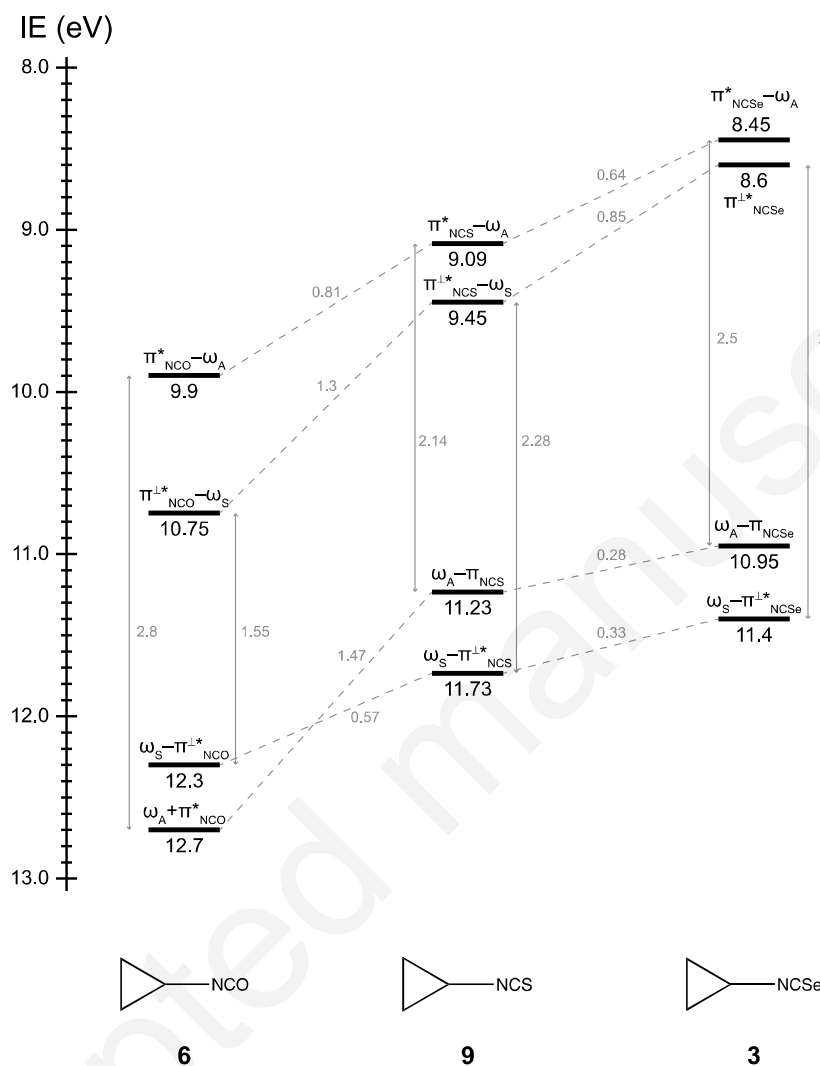


Figure 8. Comparison of first four experimental ionization energies [eV] of cyclopropyl isocyanate **6**, cyclopropyl isothiocyanate **9**⁵⁴ and cyclopropyl isoselenocyanate **3**.

The comparison of the first four experimental ionization energies of cyclopropyl isocyanate **6**, cyclopropyl isothiocyanate **9**⁵⁴ and cyclopropyl isoselenocyanate **3** shows a significant stabilizing (withdrawing) effect of oxygen atom since, as noted for vinyl and allyl derivatives, all IEs correspond to lower energy (higher IE values) than those of the sulfur or selenium -NCX functional group. The measure of the Walsh orbitals (ω_A and ω_S) interaction with -NCX moiety can be considered as an energy difference between $\pi^*_{\text{NCX}} - \omega_A$ (or $\pi^{\perp*}_{\text{NCX}} - \omega_S$) and $\omega_A - \pi^*_{\text{NCX}}$ (or $\omega_S - \pi^{\perp*}_{\text{NCX}}$). The highest value of 2.8 eV is obtained for $\pi^*_{\text{NCO}} - \omega_A / \omega_A - \pi^*_{\text{NCO}}$.

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2 π^*_{NCO} of cyclopropyl isocyanate **6** and means that Walsh orbitals in this context have the same
3 contribution as the vinyl substituent does (2.85 eV). A slightly weaker input is conferred to
4 the sulfur (2.14 eV) and selenium derivatives (2.5 eV).
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8 Finally, the three photoelectron spectra of isoselenocyanates **1-3** can be compared to
9 each other. As can be seen from the comparison of the first four experimental ionization
10 energies of vinyl isoselenocyanate **1**, allyl isoselenocyanate **2** and cyclopropyl
11 isoselenocyanate **3** (Figure 9), the vinyl and cyclopropyl isoselenocyanates present
12 similarities such as stronger interactions between the NCX functional group and the
13 substituent (vinyl and cyclopropyl, respectively), while in the case of allyl and –NCSe
14 functional groups two non-interacting moieties should be considered.
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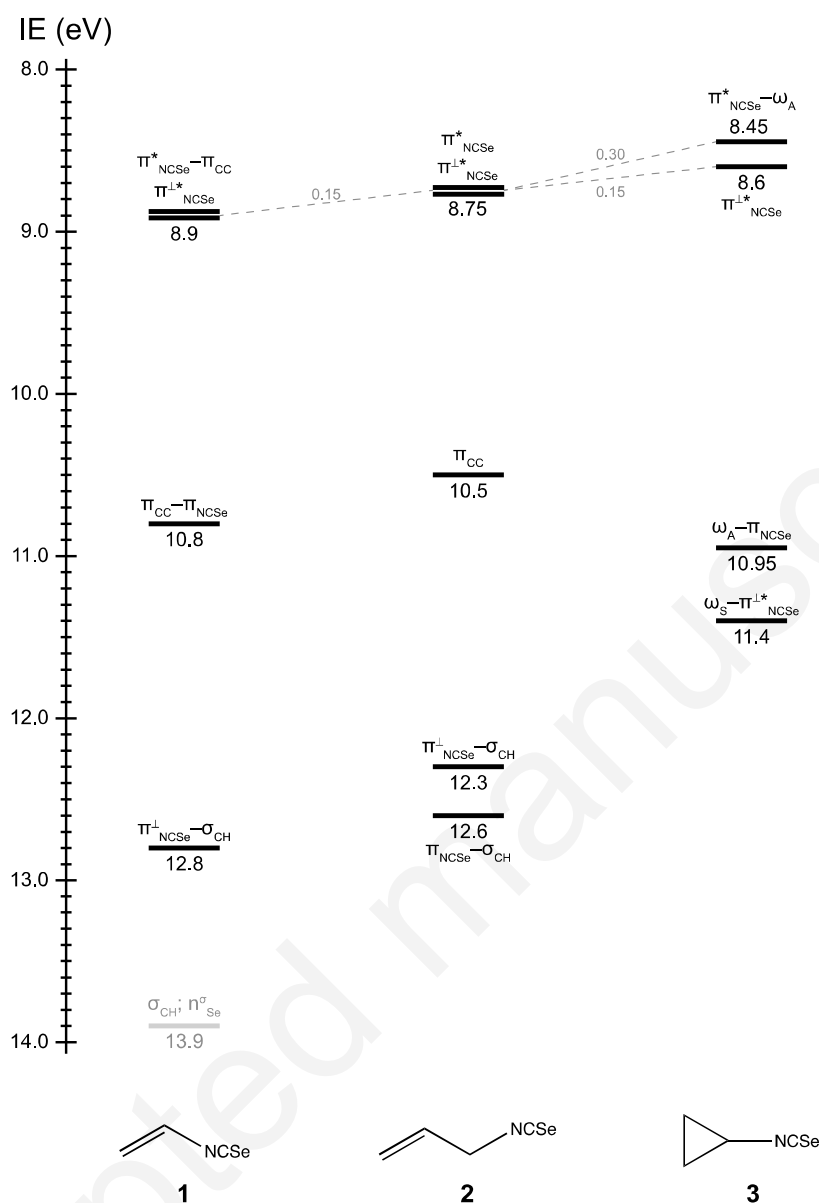


Figure 9. Comparison of first four experimental ionization energies [eV] of compounds 1-3.

3. Conclusion

For the vinyl series $\text{H}_2\text{C}=\text{CH}-\text{N}=\text{C}=\text{X}$ ($\text{X} = \text{O}, \text{S}, \text{Se}$), all IEs of selenium and sulfur derivatives are lowered in comparison with the corresponding isocyanate, showing a decrease of the strength of the vinyl substituent ($\pi_{\text{C}=\text{C}}$) interaction with the $-\text{N}=\text{C}=\text{X}$ functional group. Similar effects were observed for cyclopropyl derivatives between the pseudo-unsaturated cyclopropyl substituent and the $\text{N}=\text{C}=\text{X}$ moiety. Such an interaction between the functional groups in the allylic series was only observed for the oxygen derivative. The Figure 10 summarizes the comparisons between the first IE of these nine compounds. The influence of

the vinyl, cyclopropyl and allyl substituents on the first IE of R-NCX (X = Se, O, S) is clearly demonstrated. For X = Se, due to the weak interaction between the substituent and the -NCSe functional group, the higher lying HOMO is found for the cyclopropyl substituent. In the case of X = O, strongly interacting -NCO moiety and vinyl substituent, follow to the higher energy of HOMO in comparison with its cyclopropyl and allyl derivatives. The -NCS functional group is much less sensitive to a change of environment.

Thanks to the synthesis, theoretical calculations and photoelectron spectroscopy of the selenium derivatives, the type and extent of the interaction between the N=C=X (X = O, S, Se) group and an unsaturated (vinyl, allyl) or pseudo-unsaturated (cyclopropyl) moiety are now clarified as well as the comparison of the interactions with the substituent for each heteroatom.



Figure 10. Comparison of first experimental ionization energies [eV] of compounds **1-9**.

Supporting Information.

The SI part contains computational details (optimized geometries, energies, conformer studies) about compounds **1-9** and Tables (S1-S6) of comparison of calculated and experimental ionization energies [eV] for compounds **2, 3, 5, 6, 8, 9**.

Acknowledgment. The authors thank P. Baylère for his efficient technical assistance. J.-C. G. thanks for funding the Centre National d'Etudes Spatiales (CNES) and the Programme

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2 National Physique et Chimie du Milieu Interstellaire (PCMI) of CNRS/INSU with INC/INP
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4 co-funded by CEA and CNES.
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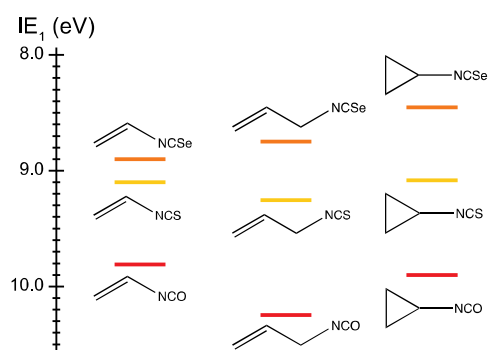
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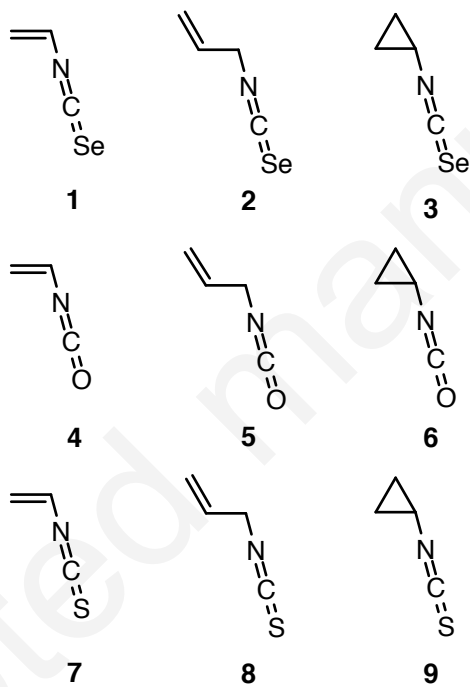
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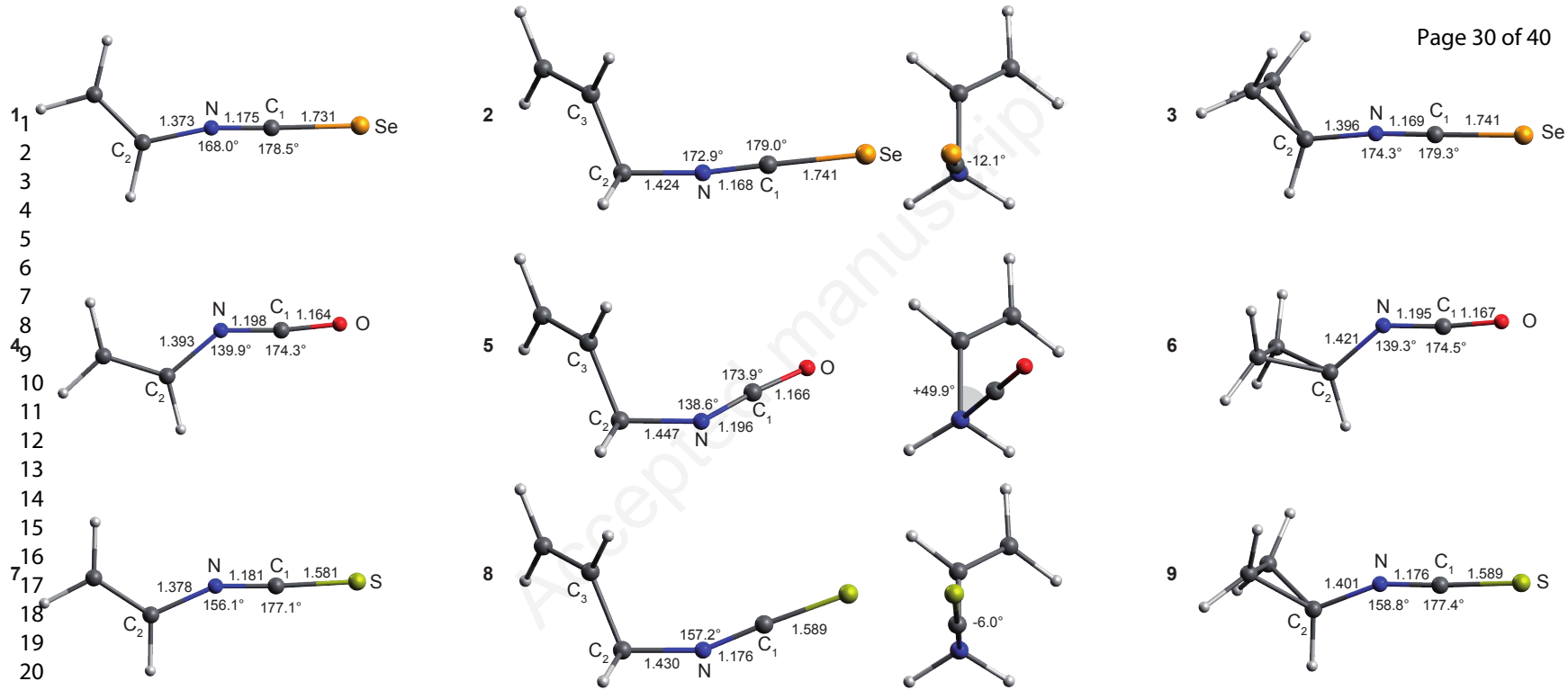
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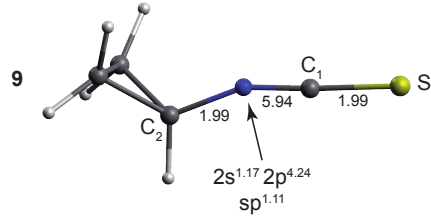
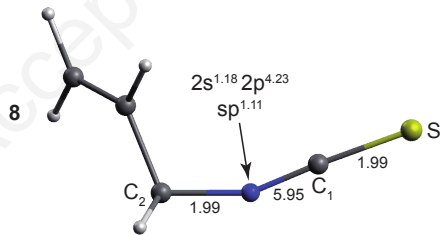
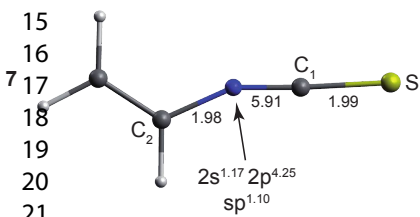
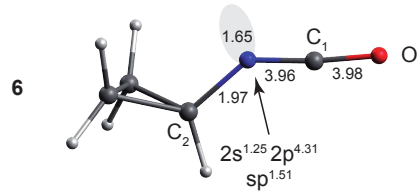
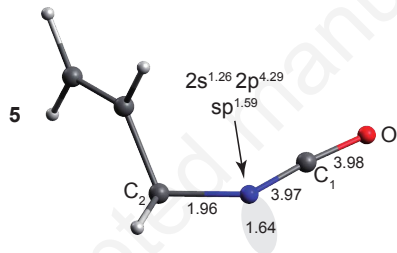
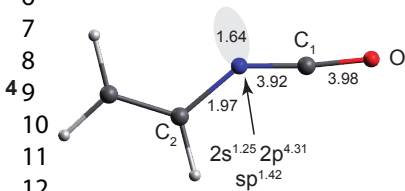
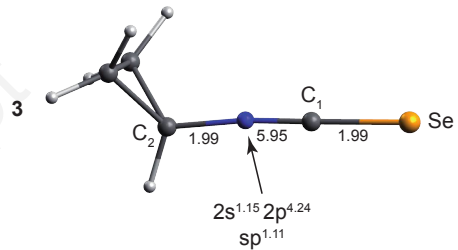
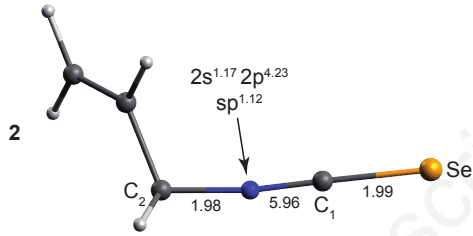
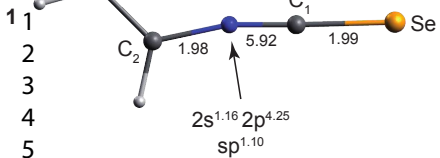
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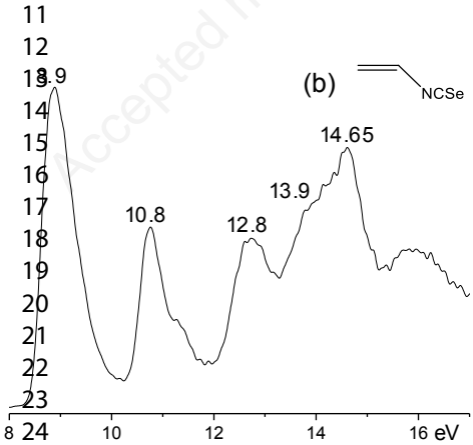
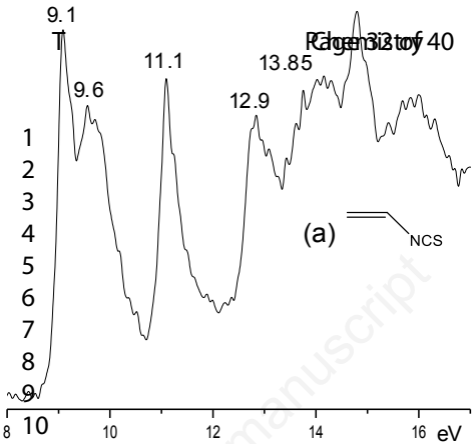


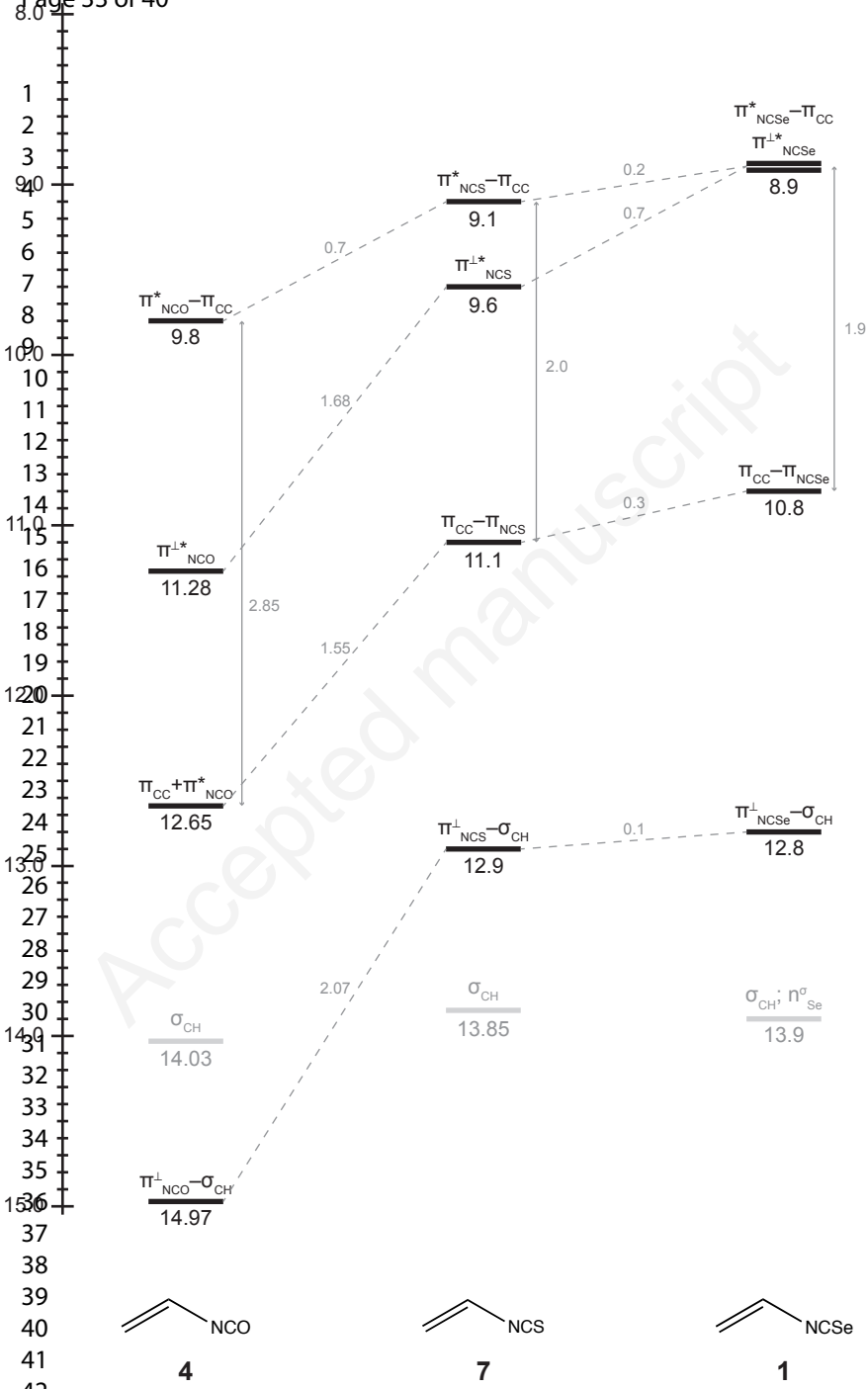
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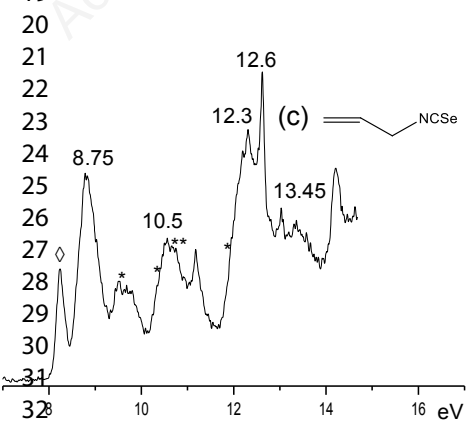
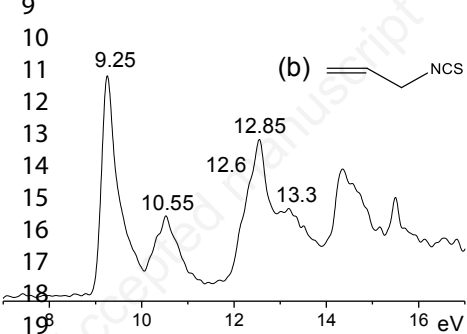
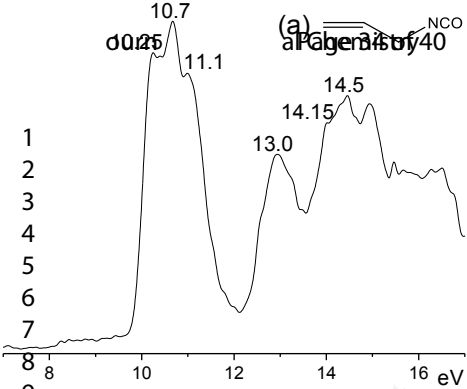


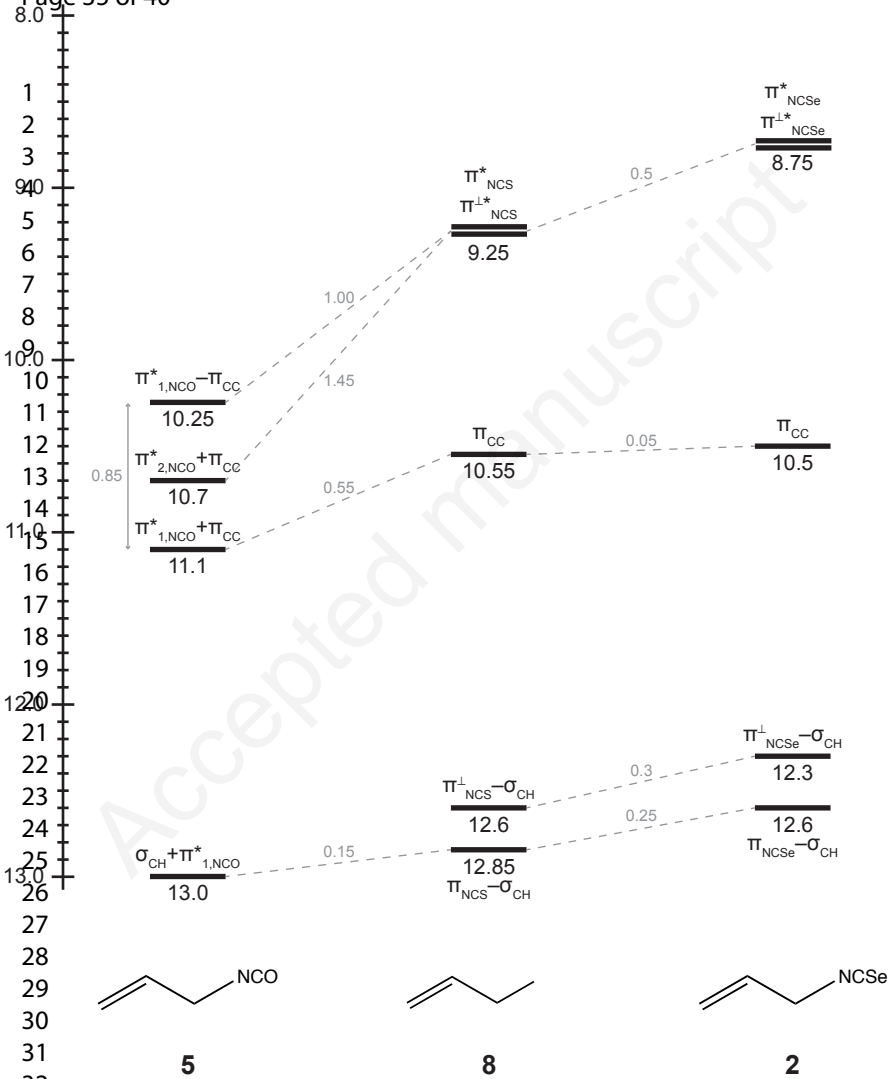


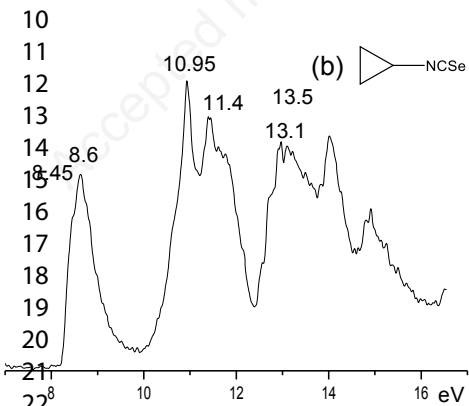
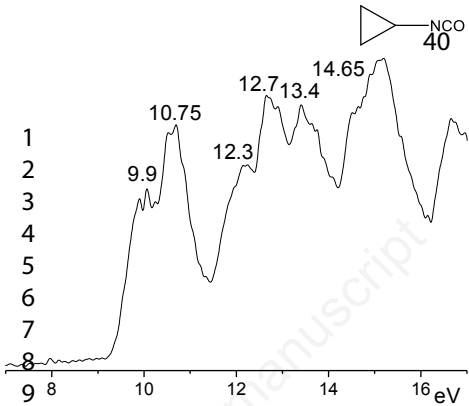


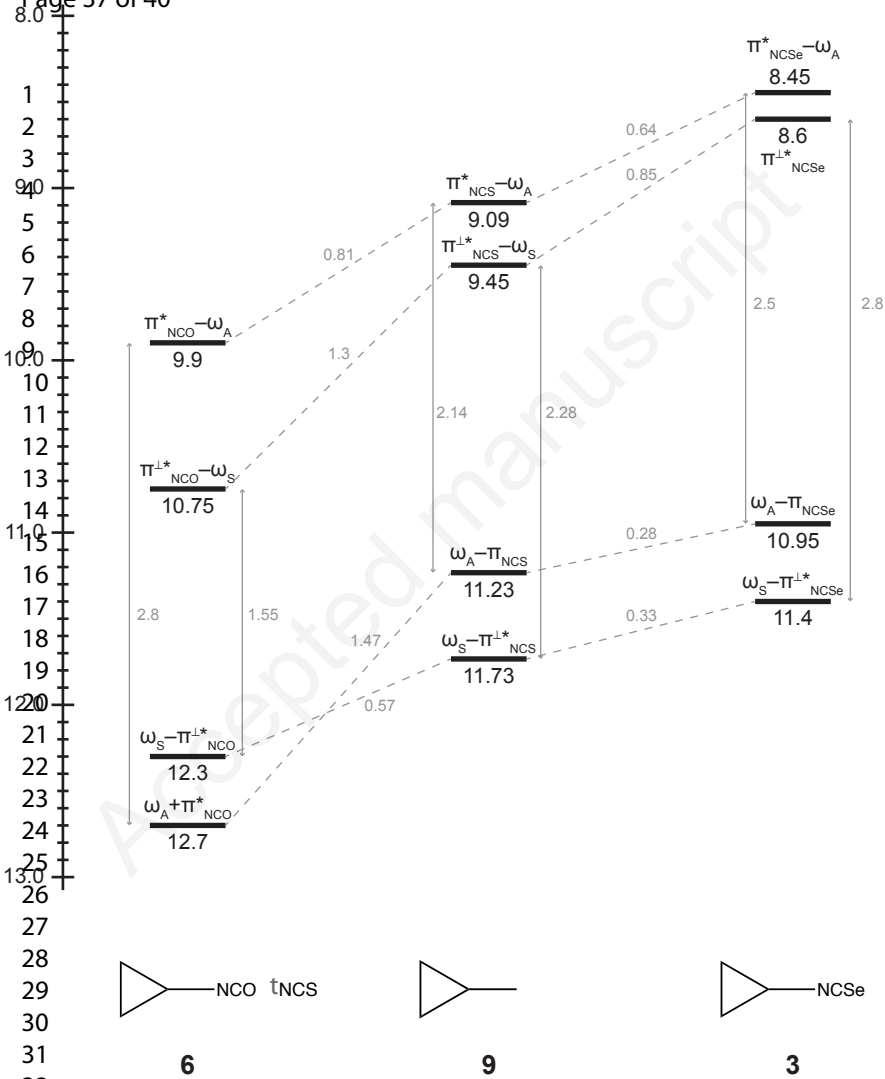


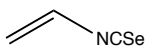
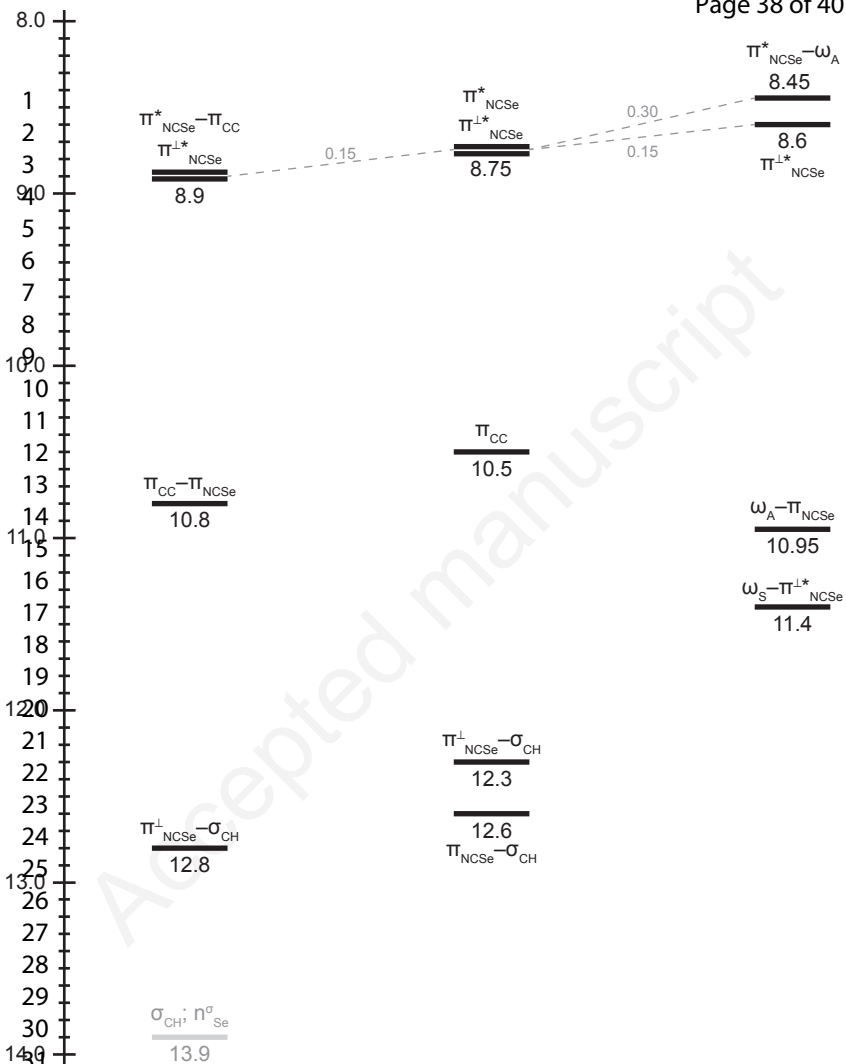




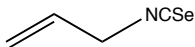




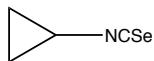




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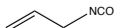
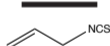
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IE_1 (eV)

