

Generation and Spectroscopic Identification of Selenofulminic Acid and Its Methyl and Cyano Derivatives (XCNSe, X = H, CH₃, NC)

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Abstract: Evidence for the existence of nitrile selenides, potential 1,3-dipolarophiles in cycloaddition reactions, has been provided by direct spectroscopic methods. The parent nitrile selenide, selenofulminic acid (HCNSe), and its methyl and cyano derivatives have been photolytically generated in an inert solid argon matrix from 1,2,5-selenadiazoles by 280, 254, and 313 nm UV irradiation, respectively, and studied by ultraviolet spectroscopy and mid-infrared spectroscopy. Ground-state geometries have been obtained from quantum-chemical calculations at the CCSD(T)/aug-cc-pVTZ level. Nitrile selenides are predicted to be linear with a relatively weak N–Se bond.

Keywords: IR spectroscopy • matrix isolation • selenium • reactive intermediates • UV/Vis spectroscopy

Introduction

Since their first indirect discovery,^[1] nitrile sulfides (XCNS) have become important transient species in various cycloaddition reactions.^[2–4] These reactions provide routes to several classes of heterocycles, among them many biologically active compounds.^[4] By analogy, nitrile selenides (XCNSe) are expected to be key intermediates in producing selenium containing heterocycles, for example, selenazoles and selenadiazoles; however, their chemistry is unexplored. No method is known to generate these species in solution yet. The existence of only one derivative, benzonitrile selenide (PhCNSe), has been unambiguously proven directly by IR and UV spectroscopy in low-temperature matrices.^[5,6] In similar experiments a UV band between 220 and 250 nm was tentatively assigned to HCNSe and CH₃CNSe, but none of the transitions of these species were identified in the IR spectra.^[6] Furthermore, it is important to note that small nitrile selenides have been generated and identified as neutral species in the gas phase of a mass spectrometer by neutralization–reionization mass spectroscopy,^[7,8] which established the existence of these species with lifetimes of at least microseconds in the dilute gas phase.

Nitrile selenides are expected to be unstable in the pure state and in solution, analogously to nitrile sulfides, thus their direct spectroscopic identification is possibly challenging. A promising method for spectroscopic detection seems

to be the generation of nitrile selenides in cold, inert noble gas matrices, in which thermal decomposition and bimolecular reactions are avoided. This is in line with the relevant nitrile sulfide chemistry, for which all of the four spectroscopically identified derivatives, HCNS,^[9] FCNS,^[10] CH₃CNS,^[11,12] and PhCNS,^[12,13] have been identified at low temperatures and in inert matrices. Possible sources of nitrile selenides could be molecules containing the CNSe linkage and a good leaving group, releasing the desired product upon UV irradiation. We have successfully applied 1,2,5-thiadiazoles as sources of nitrile sulfides recently,^[9–11] thus 1,2,5-selenadiazoles have been selected for the present study as potential sources of nitrile selenides. It is important to note that PhCNSe was generated analogously from 3,4-diphenyl-1,2,5-selenadiazole and 3,5-diphenyl-1,2,4-selenadiazole earlier.^[5,6] It is also important to note that the UV photolysis of 1,2,5-selenadiazole and 3,4-dimethyl-1,2,5-selenadiazole at 300 nm has been attempted before,^[6] but no definitive conclusion for the identity of the detected transient species could be drawn; photolabile species have been detected by UV spectroscopy, but they could not be identified by IR spectroscopy.

Due to the paucity of experimental investigations, theoretical calculations can provide information about the structure and stability of nitrile selenides. All investigated nitrile selenides (X = H, F, Cl, Br, I, NC, OH, NH₂, CH₃, CH₃S) have been calculated to be thermodynamically stable species at the G2(MP2,SVP) level.^[8] The calculated N–Se bond dissociation energies are in the range of 148–187 kJ mol^{–1}, which suggests stability at room temperature. All nitrile selenides are predicted to have a linear or a slightly bent XCNSe frame at the MP2/6-31G* level.^[8] We note, however, that the RHF wavefunction is unstable for nitrile oxides^[14] and nitrile sulfides,^[4,11] thus the same is expected for nitrile selenides, which indicates that earlier MP2 results must be treated with care.

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201103004>.

In this paper, we present an experimental study on the generation of HCNSe, CH₃CNSe, and NCCNSe in an argon matrix from 1,2,5-selenadiazoles and their IR and UV spectroscopy, as well as a quantum-chemical study on the equilibrium structure and vibrational properties.

Results and Discussion

Structure and stability of nitrile selenides: Since the inclusion of electron correlation is custom for calculations on relevant simple nitrile oxides^[14] and nitrile sulfides,^[4] the geometry of HCNSe, CH₃CNSe, and NCCNSe was calculated at the CCSD(T) level using a large, aug-cc-pVTZ, basis set. We note that the HF wavefunction is unstable for NCCNSe (RHF-UHF instability), but single point CCSD(T) and UCCSD(T) calculations provided identical total energies. The CCSD T1 diagnostic for all three molecules was 0.02. Single point CASSCF(10,10) calculations, using the CCSD(T) geometries, have indicated that apart from the main HF configuration (weight: 92, 100, and 92% for HCNSe, CH₃CNSe, and NCCNSe, respectively) there was no other important configuration. Therefore, the single reference post-HF CCSD(T) method seemed to be sufficient for describing the electronic structure.

The calculated equilibrium geometries of HCNSe, CH₃CNSe, and NCCNSe are shown in Table S1 in the Supporting Information. Calculations predict that HCNSe and NCCNSe are linear, and CH₃CNSe is a symmetric top molecule with a linear CCNSe frame. Comparing the NSe and CN bond lengths of nitrile selenides with those of molecules that have typical single/double NSe and double/triple CN bonds (H₂N–SeH/HN=Se and H₂C=NH/HC≡N), the CN bond is close to a triple bond and the NSe is between a single and a double bond (Tables S1 and S2 in the Supporting Information). Calculated bond orders (Table S1 in the Supporting Information), using the Gordy rule,^[15] for CN and NSe bonds are 2.8–3.0 and 1.4–1.9, respectively. All three molecules have a singlet electronic ground state. In the case of HCNSe the singlet is more stable than the triplet by 172 kJ mol^{−1} (see Table S3 in the Supporting Information). Concerning stability versus unimolecular decomposition, the strength of the N–Se bond, the expected weakness of the molecule, is of crucial importance. The calculated N–Se bond dissociation energies are in the range of 174–188 kJ mol^{−1} (ΔG°_{0K}) for the spin-allowed dissociation process (see Table S1). These values are approximately 25% smaller than that of nitrile sulfides,^[4] but they are high enough to predict unimolecular stability at room or slightly elevated temperatures, for example, in a boiling solvent.

Generation and identification of HCNSe: Based on our previous results on nitrile sulfides^[9–11] the narrow-band UV photolysis of 1,2,5-selenadiazole seemed to be an appropriate generation route of HCNSe. HCN is an ideal side product in the sense that it has only very low-intensity IR bands in the CN stretching region (see Table S4 in the Supporting

Information) and does not absorb in the investigated UV region.^[16] However, one has to keep in mind that some shifts of the spectroscopic transitions of the isolated HCNSe can be caused by interactions between HCN and HCNSe formed in the same matrix cage.

The UV spectrum of 1,2,5-selenadiazole in an Ar matrix is shown in Figure 1. Since nitrile sulfides could be generated by irradiating the matrix at a wavelength near the first

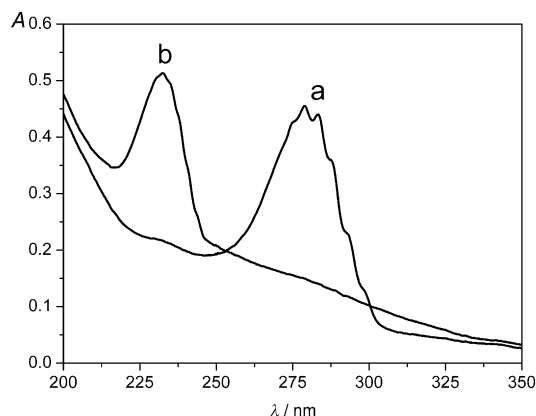


Figure 1. a) UV spectrum of the 1,2,5-selenadiazole precursor in an Ar matrix and b) the UV spectrum recorded after 10 min photolysis at 280 nm.

UV absorption band of the 1,2,5-thiadiazole precursors, the photolysis of 1,2,5-selenadiazole was examined at 254 and 280 nm. These wavelengths are at the blue tail and at the maximum intensity of the first absorption band of 1,2,5-selenadiazole. At both of these wavelengths a primary photoproduct appeared during the photolysis, with a band centred between 210 and 250 nm (see Figure 1 and Figure S1 in the Supporting Information). Both the position and the shape of this band are identical to the band published in ref. [6], which was tentatively assigned to HCNSe. During irradiation, using either the 254 or the 280 nm filter, the intensity of this band showed a maximum in time. The maximum intensity was larger, whereas the decrease rate of the band was much lower in the case of 280 nm photolysis. This is not surprising, since 254 nm is at the red tail of the primary photoproduct. Upon broad-band UV photolysis the primary photoproduct completely disappeared.

Observations in IR experiments concur with that of UV and provide unambiguous evidence of the formation of HCNSe. The difference between the IR spectra recorded before and after 280 nm photolysis is shown in Figure 2 together with the computed spectrum of HCNSe and that of HCN. (The difference IR spectrum obtained at 254 nm photolysis is shown in the Supporting Information, Figures S2, S4, and S6.) As can be seen in the Figures and from the data of Table 1 the two most intense peaks in the experimental spectrum at 3284 and 2045 cm^{−1} (with a shoulder at 2047 cm^{−1}) correlate very well with the computed CH and CN stretching fundamentals of HCNSe at 3309 and

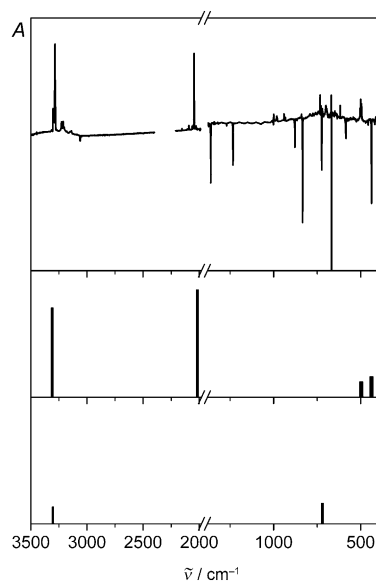


Figure 2. The experimental spectrum (top panel) obtained as the difference of the spectra of 1,2,5-selenadiazole in Ar matrix after and before photolysis at 280 nm for 30 min, the computed spectrum of HCNSe (middle panel), and the composite spectrum (experimental frequencies^[17] with computed intensities) of HCN (bottom panel).

Table 1. Experimental and calculated anharmonic vibrational frequencies ($\tilde{\nu}$, in cm^{-1}) and infrared intensities (I , in km mol^{-1}) of HCNSe.

Vibrational mode	Calculated $\tilde{\nu}^{[a]}$	Calculated $I^{[b]}$	Experimental ^[c] (Ar matrix)
$\nu_1(\sigma^+)$ CH str	3309 (3446)	318 [391]	3284 vs
$\nu_2(\sigma^+)$ C≡N str	2016 (2064)	382 [368]	2047 s, sh 2045 vs
$\nu_3(\sigma^+)$ NSe str	497 (505)	55 [38]	504 m, 500 m, 496 m
$\nu_4(\pi)$ HCN bend	439 (445)	73 [72]	not observed
$\nu_5(\pi)$ CNSe bend	348 (347)	45 [46]	not observed

[a] Anharmonic frequencies are calculated as the sum of harmonic frozen-core CCSD(T)/aug-cc-pVTZ frequencies (given in brackets) and CCSD(T)/cc-pVTZ anharmonic corrections. Isotopes: ^1H , ^{12}C , ^{14}N , ^{80}Se . [b] Calculated at the CCSD(T)/cc-pVTZ level using the anharmonic approximation. Harmonic intensities are in square brackets. [c] Due to the presence of a hydrogen cyanide molecule in the same site, the data presented might be slightly shifted compared with that of the free isolated HCNSe molecule. Some of the bands are split due to site effects.

2016 cm^{-1} , respectively. The difference between the experimental and the computed wavenumbers is only 1% for CH, and 1.5% for CN stretching. Besides the computational inaccuracy this small discrepancy could be due to matrix shift and due to the interaction of HCNSe with the HCN side product. The corresponding vibrational transitions of the H^{13}CNSe species were also observed as weak bands at 3268 and 2013 cm^{-1} , that is, shifted by -16 and -32 cm^{-1} compared with the bands of H^{12}CNSe . This is in good agreement with the computational results (see Table S5 in the Supporting Information), which predicted -18 and -33 cm^{-1} shifts, respectively.

Notably, the frequency of the CH mode of $\text{HCNS}^{[9]}$ and HCNSe is lower by 15 and 17 cm^{-1} , respectively, than that of HCN. As can be expected, the CN stretching mode is

much more affected by the NS and NSe bond formation. Compared with HCN the CN stretching mode is shifted by -58 and -48 cm^{-1} in $\text{HCNS}^{[9]}$ and HCNSe , respectively.

In addition to the CH and CN stretching fundamentals the NSe stretching is also observed at 504 , 500 , and 496 cm^{-1} . There are also weak shoulders at these peaks. This splitting is partly due to matrix effects, and as proved by computations (see Table S5 in the Supporting Information), the isotopic shift between the naturally abundant Se isotopes is also responsible for this complicated band system. The other fundamental vibrational modes are shifted much less upon Se isotope substitution.

Based on previous experimental results^[17] and our computations (see Table S4 in the Supporting Information) the weak bands of HCN could also unambiguously be identified at 3302 and 720 cm^{-1} . These peaks are relatively more intense when the precursor is photolysed at 254 nm instead of 280 nm . All the other peaks (see the complete list in Table S6 in the Supporting Information) that appeared upon photolysis are weak. Most of them could be assigned to hydrogen-bonded $\text{HCN}\cdots\text{HCN}$ dimers^[17] or to other HCN complexes, which might represent either a dimer of a different configuration or a second possible site for the dimer in the matrix.

Both UV and IR spectroscopic measurements have indicated photochemical similarity between nitrile selenides and nitrile sulfides^[9–11]; both decompose upon broad-band UV irradiation producing nitriles and nitrile dimers in the matrix cavity. Comparing the photochemical decomposition of 1,2,5-selenadiazole to that of 1,2,5-thiadiazole,^[9] the comparable evolution of the HCN monomer and dimer bands indicates that the final decomposition product of selenadiazole is Se atom.

The HCN bending transition is predicted by calculations to appear in the investigated spectral region at 439 cm^{-1} with larger intensity than that of the NSe stretching mode, however, it has not been observed down to the detection limit (400 cm^{-1}). This discrepancy might be due to the overestimation of the frequency or the intensity of this mode by computations. We note that the HCN bending transition of HCNS is observed in an Ar matrix at 405 cm^{-1} ,^[9] thus the computational overestimation is very likely. The CNSe bending is predicted to be beyond the experimentally investigated spectral range (see Table 1).

Finally, it is interesting to note that HCNSe was not identified by IR spectroscopy among the photoproducts of 1,2,5-selenadiazole earlier.^[6] It was noted, however, that the irradiation of 1,2,5-selenadiazole with 300 nm light produced sharp bands at 2044.8 and 2046.5 cm^{-1} , which concurs with our results. Our work thus indicates the possibility that these bands were incorrectly assigned to the CN radical before.

Generation and identification of CH_3CNSe : 3,4-Dimethyl-1,2,5-selenadiazole absorbs in the $240\text{--}302\text{ nm}$ UV range, and decomposes upon UV irradiation at 254 and 280 nm (see Figure 3 and Figure S8 in the Supporting Information).

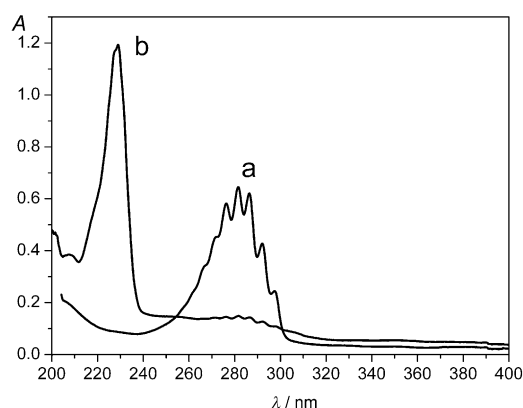


Figure 3. a) UV spectrum of the 3,4-dimethyl-1,2,5-selenadiazole precursor in an Ar matrix and b) the UV spectrum recorded after 120 min photolysis at 254 nm.

In agreement with a previous investigation, in which 300 nm irradiation was used,^[6] a single UV band centred at 229 nm appears in both cases at the expense of the absorption band of the precursor. The product has been found to be stable upon irradiation at 254 or 280 nm, in contrast to HCNSe (see above), not surprisingly, because this absorption band is slightly shifted to the blue and it is narrower than the first absorption band of HCNSe. IR investigations (see below) confirm the formation of CH_3CNSe in the photolysis, and support the assignment of the UV band to CH_3CNSe .

The difference of IR spectra recorded before and after 254 nm irradiation is shown in Figure 4. The dominating

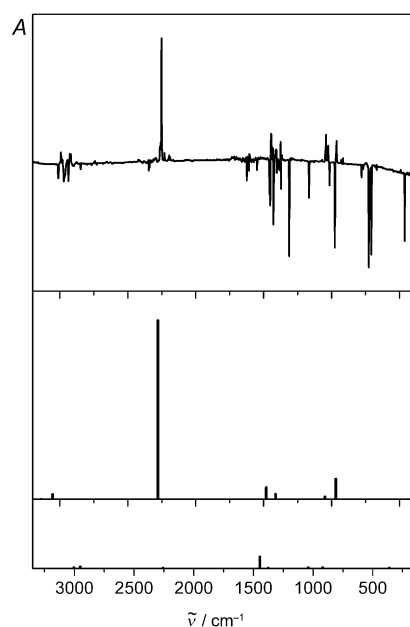


Figure 4. The experimental spectrum (top panel) obtained as the difference of the spectra of 3,4-dimethyl-1,2,5-selenadiazole in an Ar matrix after and before photolysis at 254 nm for 120 min, the computed spectrum of CH_3CNSe (middle panel), and the composite spectrum (experimental frequencies^[18] with computed intensities) of CH_3CN (bottom panel).

band of the experimental spectrum appears at 2251 cm^{-1} with a side band of almost equal in intensity at 2253 cm^{-1} . Both bands disappeared upon broad-band UV irradiation, which precludes the possibility of assigning these bands to CH_3CN . We note that the appearance of two bands at 2250 and 2252 cm^{-1} during the 300 nm photolysis of 3,4-dimethyl-1,2,5-selenadiazole were noted before, but were incorrectly assigned to CH_3CN .^[6] The position of this site-split band agrees very well with the calculated frequency of 2282 cm^{-1} for CH_3CNSe . This band is blueshifted compared with that of HCNSe, and interestingly this $+206\text{ cm}^{-1}$ experimental blueshift compares well with the $+202\text{ cm}^{-1}$ blueshift of the corresponding sulfur analogue, namely the observed difference between the CN stretching modes of CH_3CNS and HCNSe.^[9,11] There is a relatively large calculated isotope shift for this band, and weak bands at 2203 and 2201 cm^{-1} may be assigned to $^{12}\text{CH}_3^{13}\text{CNSe}$ (see Table S7 in the Supporting Information).

All vibrational modes of CH_3CNSe but the CN stretching have low IR intensity (Table 2), thus their assignment is less straightforward. Examination of the increase of IR bands as

Table 2. Experimental and calculated anharmonic vibrational frequencies ($\tilde{\nu}$, in cm^{-1}) and infrared intensities (I , in km mol^{-1}) of CH_3CNSe .

Vibrational mode	Calculated $\tilde{\nu}^{[a,c]}$	Calculated $I^{[b,c]}$	Experimental ^[d] (Ar matrix)
$\nu_1(a_1)$ CH_3 s str	2937 (3050)	7 [8]	2926 vw
$\nu_2(a_1)$ $\text{C}\equiv\text{N}$ str	2282 (2275)	293 [284]	2253 vs, 2251 vs
$\nu_3(a_1)$ CH_3 s def	1382 (1415)	8 [8]	1364 vw ^[e]
$\nu_4(a_1)$ CC str	958 (966)	33 [33]	1028 m, 1027 m, 1025 m
$\nu_5(a_1)$ NSe str	394 (397)	21 [20]	not observed
$\nu_6(e)$ CH_3 as str	(3134)	[0.5]	not observed
$\nu_7(e)$ CH_3 as def	(1483)	[19]	1431 vw ^[e]
$\nu_8(e)$ CH_3 rock	(1051)	[4]	not observed
$\nu_9(e)$ CNSe bend	(382)	[3]	not observed
$\nu_{10}(e)$ CCN bend	(142)	[4]	not observed

[a] Anharmonic frequencies are calculated as the sum of harmonic frozen-core CCSD(T)/aug-cc-pVTZ frequencies (given in brackets) and CCSD(T)/cc-pVTZ anharmonic corrections. Isotopes: ^1H , ^{12}C , ^{14}N , ^{80}Se . [b] Calculated at the CCSD(T)/cc-pVTZ level using the anharmonic approximation. Harmonic intensities are in square brackets. [c] Differences between the anharmonic corrections for the corresponding degenerate vibrational modes are unacceptably large. [d] Due to the presence of an acetonitrile molecule in the same site, the data presented might be slightly shifted compared with that of the free isolated CH_3CNSe molecule. Some of the bands are split due to site effects. [e] Very weak bands, tentative assignment.

a function of irradiation time during the 254 and 280 nm irradiation and the decrease during the broad-band UV irradiation, as well as the correlation with the CN stretching band, has helped the identification of the bands of CH_3CNSe . According to this the intensity of bands at 2926, 1431, 1364, 1028, 1027, and 1025 cm^{-1} has changed at the same rate during the photolysis, suggesting that they belong to the same species. Band positions and relative IR intensities are in acceptable agreement with calculated anharmonic frequencies and IR intensities of CH_3CNSe (see Table 2). According to our calculations the CH_3 antisymmetric

stretching has very low IR intensity and the NSe stretching, CNSe bending, and CCN bending are out of the investigated region, thus they are not observed in the spectrum.

The side photolysis product, CH_3CN , has very low IR transition intensities (see Table S4 in the Supporting Information). Since it forms together with other photolysis products in the same matrix cage, its infrared frequencies are perturbed owing to weak intermolecular interactions and weak complex formations depending on the orientation of photoproducts. Thus, it is not surprising that not only the CH_3CN monomer, but its dimer could be identified among the weak bands, especially after broad-band UV irradiation. The full list of IR bands, likely to belong to CH_3CN and its complexes, are listed in Table S8 of the Supporting Information. The assignment is based on literature data,^[18] and on the comparison of IR spectra before and after broad-band UV irradiation, that is, before and after photobleaching CH_3CNSe . These bands were also observed during the photolysis of the corresponding sulfur analogue 3,4-dimethyl-1,2,5-thiadiazole.^[11] The identity of other low intensity bands (see the full list in Table S8 in the Supporting Information) remains unknown, and they might belong to other side products or impurities.

Generation and identification of NCCNSe: Since the first electronic absorption band of 3,4-dicyano-1,2,5-selenadiazole (see Figure 5) is redshifted by about 25 nm compared with the first band of 1,2,5-selenadiazole, the dicyano substituted precursor could be irradiated at longer wavelength, at 313 nm, than 1,2,5-selenadiazole. Even at this wavelength, only transient formation of a photoproduct, identified as NCCNSe by IR (see below), could be observed. The UV band assignable to NCCNSe appeared only as a shoulder at the blue end of the first absorption peak of 3,4-dicyano-1,2,5-selenadiazole (see Figure 5) and disappeared together with the band of the precursor with longer irradiation times (see Figure S11 in the Supporting Information). The UV spectrum of NCCNSe could be obtained by subtracting the appropriately scaled UV spectrum of the precursor from spectrum recorded after relatively short (≈ 30 mins) irradiation at 313 nm. As can be seen in Figure 5, the first absorption band of NCCNSe is about 50 nm redshifted with respect to the first band of HCNSe, explaining the photolability of this species at 313 nm irradiation. The NCCN side product does not absorb in the investigated UV region.^[19]

IR investigations unambiguously identified NCCNSe as the transient species during 313 nm irradiation. It is fortuitous that the NC and CN stretching transitions of NCCNSe have outstandingly large IR intensity, even larger than that of HCNSe and CH_3CNSe (see Table 3), and the NCCN side product has very low intensity (Table S4 in the Supporting Information). These transitions are dominant in the spectrum recorded after about 30 min irradiation at 313 nm (see Figure 6), even if NCCNSe is also decomposing at this wave-

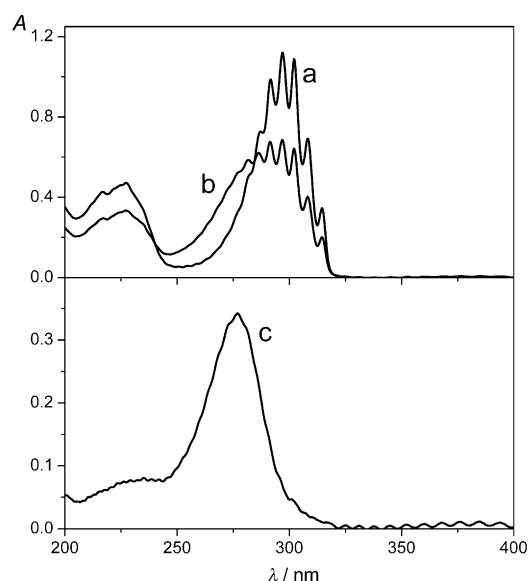


Figure 5. a) UV spectrum of the 3,4-dicyano-1,2,5-selenadiazole precursor in an Ar matrix and b) the UV spectrum recorded after 30 min photolysis at 313 nm. c) The difference between spectra a) and b).

Table 3. Experimental and calculated anharmonic vibrational frequencies ($\tilde{\nu}$, in cm^{-1}) and infrared intensities (I , in km mol^{-1}) of NCCNSe.

Vibrational mode	Calculated $\tilde{\nu}^{[a]}$	Calculated $I^{[b]}$	Experimental ^[c] (Ar matrix)
$\nu_1(\sigma^+)$ N $\equiv$ C str ^[d]	2222 (2262)	671 [785]	2232 vs, 2221 vs, 2216 m, sh
$\nu_2(\sigma^+)$ C $\equiv$ N str ^[d]	2087 (2121)	355 [371]	2103 s, 2094 s
$\nu_3(\sigma^+)$ CC str	995 (1000)	60 [64]	1022 w, 1014 w, 1005 w, sh
$\nu_4(\sigma^+)$ NSe str	398 (405)	30 [30]	not observed
$\nu_5(\pi)$ NCC bend	412 (411)	1 [0.5]	not observed
$\nu_6(\pi)$ CNSe bend	350 (354)	18 [19]	not observed
$\nu_7(\pi)$ CCN bend	96 (97)	8 [8]	not observed

[a] Anharmonic frequencies are calculated as the sum of harmonic frozen-core CCSD(T)/aug-cc-pVTZ frequencies (given in brackets) and CCSD(T)/cc-pVTZ anharmonic corrections. Isotopes: ^{12}C , ^{14}N , ^{80}Se . [b] Calculated at the CCSD(T)/cc-pVTZ level using the anharmonic approximation. Harmonic intensities are in square brackets. [c] Due to the presence of a dicyanogen molecule in the same site, the data presented might be slightly shifted compared with that of the free isolated NCCNSe molecule. The bands are split due to site effects. [d] NC and CN stretchings are strongly mixed. Note that the alternative notation of the CN modes is in-phase and out-of-phase CN vibrations.

length. Both of these peaks are strongly split due to site effects. The NC stretching is observed at 2232 and 2221 cm^{-1} with a shoulder at 2216 cm^{-1} , whereas the CN stretching is observed at 2103 and 2094 cm^{-1} . The agreement between the experimental and the computed spectrum is excellent regarding both the positions (computed at 2222 and 2087 cm^{-1}) and the relative intensities of these and other small intensity peaks. The assignment is also supported by the small intensity peaks at 2200 and 2192 cm^{-1} corresponding to the $\text{N}^{13}\text{C}^{12}\text{CNSe}$ and the $\text{N}^{12}\text{C}^{13}\text{CNSe}$ species. In detail, the experimental -32 and -29 cm^{-1} shifts of these latter small intensity bands, compared to the two site-split NC stretching band of $\text{N}^{12}\text{C}^{12}\text{CNSe}$, agree very well with the computed -31 and -23 cm^{-1} isotopic shifts of the NC

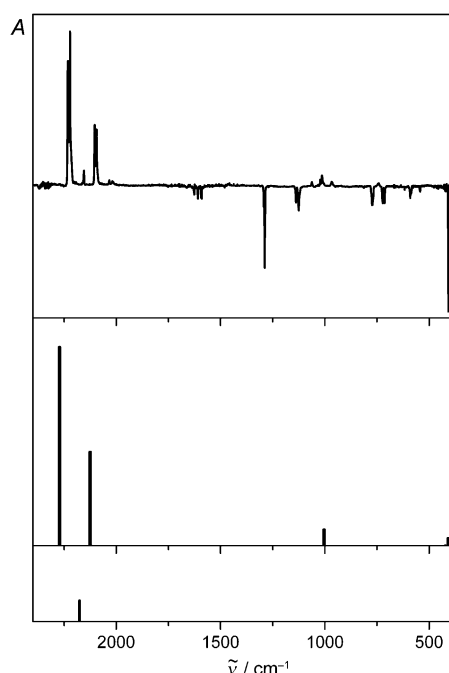


Figure 6. The experimental spectrum (top panel) obtained as the difference of the spectra of 3,4-dicyano-1,2,5-selenadiazole in an Ar matrix after and before photolysis at 313 nm for 120 min and the computed spectra of NCCNSe (middle panel) and NCCN (bottom panel).

stretching in $\text{N}^{13}\text{C}^{12}\text{CNSe}$ and $\text{N}^{12}\text{C}^{13}\text{CNSe}$, respectively (see the details in Table S9 of the Supporting Information). Similarly, the very weak bands at 2073 and 2068 cm^{-1} are shifted from the site-split band pairs of the CN stretching band of $\text{N}^{12}\text{C}^{12}\text{CNSe}$ by -30 and -26 cm^{-1} , and the computed isotopic shifts of the CN stretching of $\text{N}^{13}\text{C}^{12}\text{CNSe}$ and $\text{N}^{12}\text{C}^{13}\text{CNSe}$ are -23 and -30 cm^{-1} , respectively. (This means that both the CN and the NC stretching bands of $\text{N}^{13}\text{C}^{12}\text{CNSe}$ and $\text{N}^{12}\text{C}^{13}\text{CNSe}$ are overlapped, the splitting is due to a site effect.) In addition to the CN stretching transitions the weak site-split transition of the CC stretching can be also unambiguously assigned at 1022 , 1014 , and 1005 cm^{-1} . According to computations, the other four fundamental vibrational transitions have small molar absorptions or are below the detection limit (400 cm^{-1}), hence these modes could not be experimentally observed (see Table 3).

Although the molar absorption of the CN stretching of NCCN is more than three orders of magnitude smaller than that of NCCNSe (see Table S4 in the Supporting Information), the antisymmetric CN stretching of NCCN transition can be identified at 2155 cm^{-1} . This clearly indicates that NCCN is present in the matrix in a much larger amount than NCCNSe. NCCN is not only the side product of the primary photodecomposition of 3,4-dicyano-1,2,5-selenadiazole, but the decomposition product of NCCNSe, too. Besides transitions of NCCNSe and NCCN only a few, very weak bands (see the list in Table 10 in the Supporting Information) have appeared after irradiation at 313 nm , the identities of which are not clear.

Conclusion

The HCNSe, CH_3CNSe , and NCCNSe molecules were identified in a cryogenic argon matrix, following UV photolysis of appropriate 1,2,5-selenadiazoles. Nitrile selenides are photolabile and the selection of the proper wavelength for photodecomposition of selenadiazoles was of crucial importance. The structure of nitrile selenides was obtained from *ab initio* calculations, and the molecular frame was confirmed as linear. Although the N–Se bond is relatively weak, it is strong enough to support application of these species at room or slightly elevated temperatures.

There is a long standing interest in new dipolarophiles in cycloaddition chemistry, thus a major outcome of this research is not only the proof of the existence of nitrile selenides, but the synthetic route revealed. We expect that the generation of nitrile selenides is feasible not only in an inert matrix, as we discussed, but in solution in the presence of an appropriate dipolarophile reagent. This research, we believe, has thus opened the door for future applications.

Experimental Section

The 1,2,5-selenadiazole, 3,4-dimethyl-1,2,5-selenadiazole, and 3,4-dicyano-1,2,5-selenadiazole precursors were synthesized according to known literature methods,^[8,20,21] from ethylenediamine, dimethylglyoxime, and diaminomaleonitrile, respectively, with selenium dioxide. We note however that the yield for 1,2,5-selenadiazole and 3,4-dimethyl-1,2,5-selenadiazole is much lower than was published, ca. 0.5 and 5%, respectively. Starting materials were commercial products (Aldrich). The purity of precursors was checked by NMR and IR spectroscopies.

The matrix isolation setup has been described in detail elsewhere. The degassed 1,2,5-selenadiazole precursor was premixed in a glass vacuum line with Ar (Messer, 99.9997%) in a 1:1000 ratio. Due to low volatility, the other two precursors were placed into a sample container that was directly attached to the sample inlet of the matrix isolation setup. During the matrix deposition 3,4-dimethyl-1,2,5-selenadiazole and 3,4-dicyano-1,2,5-selenadiazole were held at 0 and 36°C , respectively, and the sample vapour was mixed with argon just before the cold window. The gas mixtures were deposited onto an 8 K CsI window for IR, and onto an 8 K or a 12 K quartz window for UV/Vis spectroscopic measurements. The flow rate was regulated with an MKS flow controller system, and maintained at ≈ 1.2 and $0.3\text{ cm}^3\text{ min}^{-1}$ for IR and UV measurements, respectively. A Cathodeon HPK 125 W high-pressure mercury lamp and an Oriel 66057 xenon lamp were used as photolysis sources. The deposited matrix was irradiated through a quartz window and an interference filter (254 or 313 nm filter for Hg lamp or 280 nm filter for Xe lamp). For broad-band UV photolysis no filter was used. The interference filters had a full width at half height of 10, 25, and 10 nm at 254, 280, and 313 nm, respectively. Infrared spectra were recorded on a Bruker IFS 55 FTIR spectrometer at 1 cm^{-1} resolution. Absorption UV/Vis spectra were recorded with a Varian Cary3E spectrometer, with a 1 nm spectral band width.

Quantum chemical calculations were performed by using the ACES2^[22] program package. Equilibrium geometries and harmonic vibrational frequencies were calculated at the CCSD(T)^[23]/aug-cc-pVTZ^[24] level. Anharmonic vibrational corrections, within the framework of second-order vibrational perturbation theory,^[25] were obtained at the CCSD(T)/cc-pVTZ level. The core electrons were not correlated (fc) in the calculations.

Acknowledgements

We thank the European Union and the European Social Fund for financial support to the project under the grant agreement no. TÁMOP 4.2.1./B-09/1/KMR-2010-0003, and the Hungarian Scientific Research Fund (grant no. OTKA K101164 and K75877).

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Received: September 24, 2011
Published online: January 30, 2012