The [2C, 2N, S] and the [2C, 2N, Se] systems were investigated by quantum chemical computations and matrix isolation IR spectroscopy. For both systems nine isomers were computationally investigated, for which harmonic and anharmonic vibrational wavenumbers and infrared (IR) intensities were calculated using the CCSD(T)/aug-cc-pVTZ level of theory. The results show that each of the isomers have two or more detectable bands in the mid IR region, which have one or two orders of magnitude larger intensity compared to the IR intensity of the most intense bands of the most stable NCSCN and NCSenCN isomers. It follows that if the most stable isomers can be detected, then the other previously unobserved isomers generated from NCSCN or NCSenCN should also be detectable with IR spectroscopy. UV spectra were also computed for each isomer at the TD-DFT B3LYP/aug-cc-pVTZ level of theory. These computations showed that the most stable isomers (NCSCN and NCSenCN) can absorb the UV radiation around 250 nm, and the irradiation may promote photoisomerization. This means that if the initial isomers are irradiated by narrow-band UV radiation, new isomers may be generated, which likely decompose by irradiating broad-band UV radiation.

The two most stable isomers, sulphur dicyanide (NCSCN) and selenium dicyanide (NCSenCN), were prepared following literature methods. The matrix isolation IR spectra of these molecules in Ar and Kr were measured for the first time. As a result of a selective 254 nm-irradiation of the deposited matrices some new bands appeared in the IR spectra, while the intensity of the bands of NCSCN or NCSenCN were decreased at the same time. Irradiation of the matrices with broad-band UV light decreased the intensity of the bands corresponding to the deposited isomers and some of the bands appeared on the 254 nm-irradiation. On the basis of the analysis of the formation rates of the different bands upon 254 nm photolysis and by comparison with the results of the quantum chemical calculations these bands could be assigned to new isomers. In the case of sulphur analogue NCSNC and NCNCS were unambiguously identified, and for selenium analogue the formation of NCSenNC and NCNCSen isomers were observed.