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On the Bonding of Selenocyanates and Isoselenocyanates and Their Protonated Derivatives

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Abstract: The structure, bonding, and protonation of NCSeX and XNCSe (X = Me, F, Cl, Br) derivatives has been investigated at the B3LYP/6–311++G(3df,2p)//B3LYP/6–31+G(d,p) level of theory. Three different approaches, namely, ELF, AIM, and NBO indicate that three main factors are responsible for the enhanced stability of the selenocyanates with respect to the isoselenocyanates when the substituents are halogens, whereas for alkyl substituents, it is the other way around: (a) the Se–X (X = F, Cl, Br) bonds are much stronger than the Se–X (X = Me); (b) the N–X (X = F, Cl, Br) bonds are much weaker than the N–X (X = Me) ones; (c) on going from the selenocyanates to the isoselenocyanates, when the substituents are halogen atoms, there is a significant weakening of the CN bond, which becomes essentially a double bond, whereas upon methyl substitution the CN bond retains its triple bond character. The same stability trends are observed for the corresponding N-protonated species. More importantly, the calculated stability differences are rather similar to those obtained for the neutral compounds, so that selenocyanates and isoselenocyanates exhibit rather similar basicities in the gas phase. Both types of isomers behave as gas-phase nitrogen bases.

Introduction

The selenocyanate group, SeCN, as the corresponding sulfur analogue, has the possibility to bond through selenium or nitrogen. As for the thiocyanate group^{1,2} both modes of coordination, XNCSe and NCSeX, are known when X is an alkyl group.^{3–8} As a matter of fact alkyl isoselenocyanates are commonly used in organic synthesis,^{9,10} and many of these derivatives have been spectroscopically characterized.^{4,8} Recently, the generation of the isocyanoselenenic acid radical cation, HNCSe⁺, from a dissociative ionization of selenourea in the gas phase has been reported.¹¹ However, the only known compounds in the gas phase when the substituent is a halogen atom, again in parallel to the sulfur analogues,^{12–15} are those in which the halogen is attached to the Se atom,^{16,17} whereas those in which the halogen is attached to the

N atom are not experimentally known. These findings and the fact that, although selenium derivatives have received significant attention in the past decade,^{18–48} many questions on their chemistry and bonding are still open, prompted us to undergo a study on the bonding and relative stabilities of substituted selenocyanates and isoselenocyanates, when the substituent is a methyl group, as the simplest case of alkyl group, and when the substituent is F, Cl, and Br.

We have also considered it of interest to investigate the effect that the protonation of these systems have on their bonding and, as a consequence, on the relative stabilities of selenocyanates with respect to isoselenocyanates.

Computational Details

The geometries of the selenocyanates and isoselenocyanates included in this study, and those of their protonated species have been optimized using the B3LYP density functional theory (DFT) approach associated with a 6–31+G(d,p) basis set expansion. This method, which includes Becke's three parameter nonlocal hybrid exchange potential⁴⁹ and the

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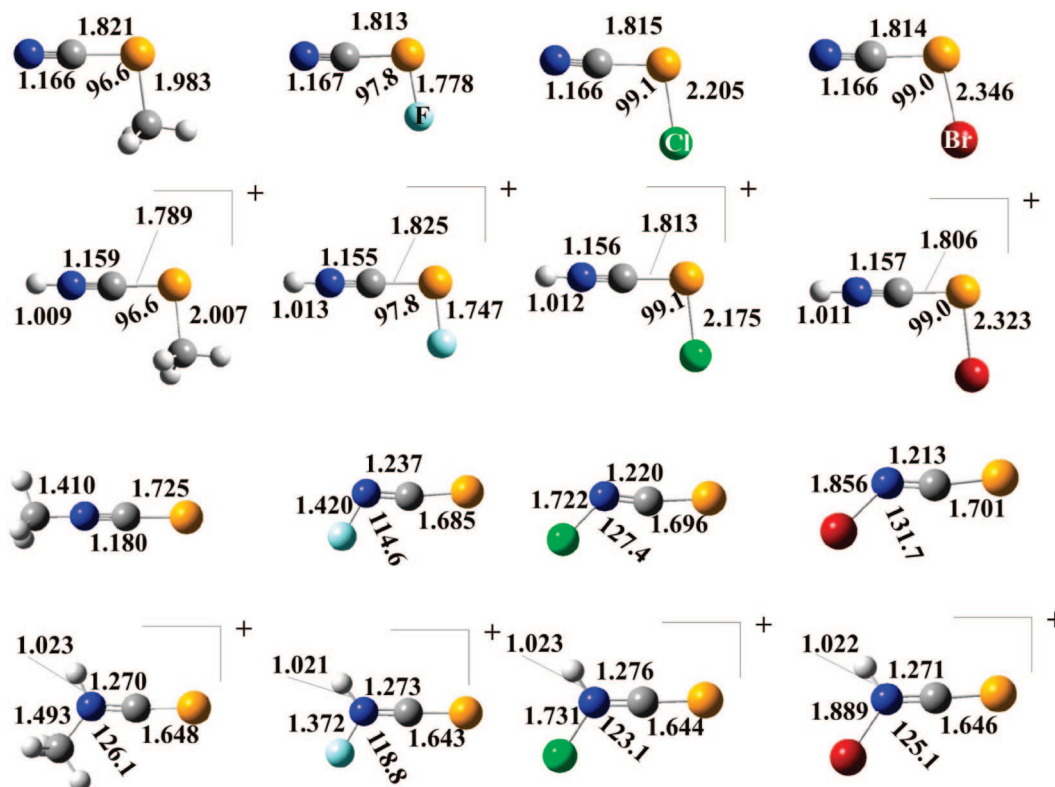


Figure 1. B3LYP/6-31+G(d,p) optimized geometries for selenocyanates and isoselenocyanates and their N-protonated species. Bond lengths are in angstroms, and bond angles are in degrees.

nonlocal correlation functional of Lee, Yang, and Parr,⁵⁰ has been successfully used for the treatment of other Se-containing compounds.^{51–53} To get reliable relative energies, final energies were obtained in single-point calculations using a 6-31++G(3df,2p) basis set. Harmonic vibrational frequencies were evaluated at the same level of theory used for the geometry optimizations to classify the stationary points found as local minima and to evaluate the thermal corrections necessary to obtain the free energies at 298.2 K.

The bonding was analyzed primarily by using the Becke and Edgecombe electron localization function⁵⁴ (ELF) topological approach.⁵⁵ ELF has been originally conceived as a local measure of the Fermi hole curvature around a reference point within the Hartree–Fock approximation, another interpretation in terms of “local excess of kinetic energy due to Pauli principle” was further proposed by Savin et al.⁵⁶ legitimating the calculation of the function with Kohn–Sham orbitals. More recently, it was shown that the ELF kernel can be rigorously derived by considering the number of same spin pairs contained in a sample around the reference point.^{57,58} Thanks to a cosmetic Lorentz transform, ELF is confined in the [0,1] interval; 1 corresponds to regions dominated by an opposite spin pair or by a single electron, whereas low values are found at the boundaries between such regions. The partition of the molecular space is carried out by the gradient dynamical technique, which yields basins of attractors closely related to Gillespie’s electronic domains which are a generalization of the ideas of Lewis. The valence shell of a molecule consists of two types of basin: polysynaptic basins (generally disynaptic), which belong to two atomic valence shells, and the monosynaptic ones, which belong to only one valence shell and

which qualitatively correspond to nonbonding valence density. The valence basins are labeled by V followed by a list of the atomic symbols of the centers of the valence shells, that is, V(A) and V(A,B) for a monosynaptic and a disynaptic basin. The basin populations and the associated covariance matrix are calculated by integration of the one electron and pair densities over the volume of the basins enabling a phenomenological interpretation of the population analysis in terms of the superposition of mesomeric structures.⁵⁹

ELF grids and basin integrations have been computed with the TopMod package.⁶⁰ The ELF isosurfaces have been visualized with the Amira 3.0 software.⁶¹ The atoms in molecules (AIM) theory,⁶² based in a topological analysis of the electron density, is a complementary tool for the investigation of bonding characteristics. In the framework of this approach, we have located the bond critical points (BCP) of each compound because the electron density at these points offers quantitatively valid information on the strength and the multiple bond character of the linkage. Moreover insights on the delocalization in terms of delocalization indexes⁶³ can be obtained by a covariance analysis of the atomic populations. This question can be also investigated by evaluation of the Wiberg bond orders⁶⁴ in the framework of the natural bond orbital (NBO) approach,⁶⁵ which also permits to estimate the weights of the different resonant structures contributing to the stability of the system through the natural resonance theory (NRT) as implemented in the NBO-5.0 suite of programs.⁶⁶ On the other hand, some further insight into details of the bonding can be gained by means of a second-order perturbation analysis of the Fock matrix, which usually provides information on the interactions between occupied and empty molecular orbitals. All

Table 1. Proton Affinities (PA, kJ mol⁻¹), Gas-Phase Basicities (GB, kJ mol⁻¹), and Relative Free Energies ($\Delta\Delta G$, kJ mol⁻¹)

compound	PA	GB	$\Delta\Delta G$ (neutral)	$\Delta\Delta G$ (protonated)
NCS ₂ F	745.8	714.6	0.0	0.0
FNCSe	751.2	719.9	173.8	168.5
NCS ₂ Cl	766.1	734.9	0.0	0.0
ClNCSe	757.3	725.6	100.3	109.6
NCS ₂ Br	775.8	744.5	0.0	0.0
BrNCSe	765.3	733.9	91.8	102.5
NCS ₂ Me	813.6	782.9	0.0	0.0
MeNCSe	791.7	759.0	-23.3	0.6

Table 2. ELF Valence Basin Populations for Selenocyanates and Isoselenocyanates

CNSeX						
X	V(Se)	V(Se,X)	V(Se,C)	V(C,N)	V(N)	V(X)
F	2 × 2.35		2.19	2 × 2.16	3.24	2 × 3.79
Cl	2 × 2.38	0.90	2.16	2 × 2.17	3.25	2 × 3.33
Br	2 × 2.42	0.92	2.17	2 × 2.16	3.26	2 × 3.44
CH ₃	2 × 2.40	1.43	2.15	2 × 2.30	3.29	

XCNCSe						
X	V(Se)	V(N,X)	V(Se,C)	V(C,N)	V(N)	V(X)
F	2 × 2.69	0.51	1.60 1.51	2 × 1.56	3.12	2 × 3.43
Cl	2 × 2.77	0.98	1.50 1.56	2 × 1.58	2.98	2 × 3.21
Br	2 × 2.79	0.92	1.35 1.64	2 × 1.60	3.0	2 × 3.33
CH ₃	5.87	1.82	2.89	3 × 1.85		

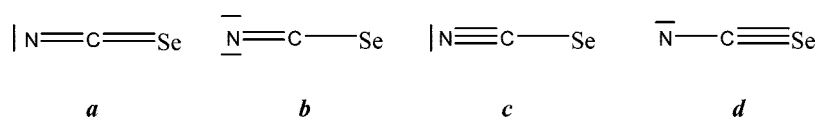
these bonding analysis have been carried out at the same level used for the geometry optimization.

Results and Discussion

The optimized geometries of the different compounds under investigation and their most stable protonated species are given in Figure 1. The calculated total energies are summarized in Table S1 of the Supporting Information.

Relative Stability and Protonation. Although protonation at the halogen, selenium, and nitrogen atoms have been considered, in all cases, for both selenocyanates and isoselenocyanates, nitrogen protonation is by far the most favorable process, so in what follows we will refer exclusively to the nitrogen protonated species. The calculated proton affinity and gas-phase basicity, defined as the negative of the enthalpy and free energy for reaction 1, respectively, are given in Table 1. This table also includes the relative stability of the isoselenocyanates with respect to the analogue selenocyanates.

Scheme 1



The first conspicuous fact is that halogen selenocyanates are systematically more stable than the corresponding isoselenocyanate isomer, similar to what has been reported before for the corresponding thio-derivatives.^{15,17} The opposite is found for the methyl derivative, where the isoselenocyanate isomer is predicted to be 23.3 kJ mol⁻¹ more stable than the selenocyanate one. The stability gap decreases in the order F > Cl > Br. Importantly, the same stability trends are observed for the corresponding N-protonated species, with the exception of the methyl derivative. For the halogen derivatives, the stability gap between isoselenocyanate and selenocyanate forms is rather similar to that calculated for the neutral forms, and as a consequence, both isoselenocyanate and selenocyanate halogen derivatives exhibit rather similar proton affinities and gas-phase basicities. For the methyl derivatives, both protonated forms are almost degenerate, and since the neutral isoselenocyanate is ~23 kJ mol⁻¹ more stable than the selenocyanate, its PA is about 23 kJ mol⁻¹ smaller.

Bonding Analysis of the Neutral Compounds. To gain some insight into the origin of the stability trends discussed in the previous section, it is necessary to carry out an analysis of the bonding similarities and dissimilarities of both families of compounds. Table 2 presents the valence basin populations of both series of compounds.

The bonding of the CNSe moiety in both families of compounds could be described, in principle, in terms of the superposition of the four mesomeric structures depicted in Scheme 1.

The values in Table 2, indicate that for the selenocyanates, the characteristics of the CN and CSe bonds are almost independent of the substituent and point to a significant contribution of the mesomeric form **c**, as reflected in the population of the V(C,N) basin. The population of the V(C,Se) basin clearly indicates that the contribution of mesomeric form **a**, although small is not negligible. In agreement with this description, the weight of these mesomeric forms estimated by means of the NRT approach are about 87% and 11% for forms **c** and **a**, respectively, with negligible contributions from form **b**. The NRT result is not apparently fully consistent with the ELF population of the V(N) basin which requires that the weights of formally ionic structures such as **b** to be greater than 50%. However, the NRT mesomeric structures being of the Coulson–Fisher type are polarized and therefore implicitly account for the ionic component. Also consistent with the ELF populations, the weights of these forms are practically independent of the substituent, as well as the Wiberg bond orders, that for the CN bond is 2.81 and for the CSe bond, 1.12. As expected, it can be observed that in the selenocyanate derivatives the ionic character of the Se–X (X = F, Cl, Br) bond decreases

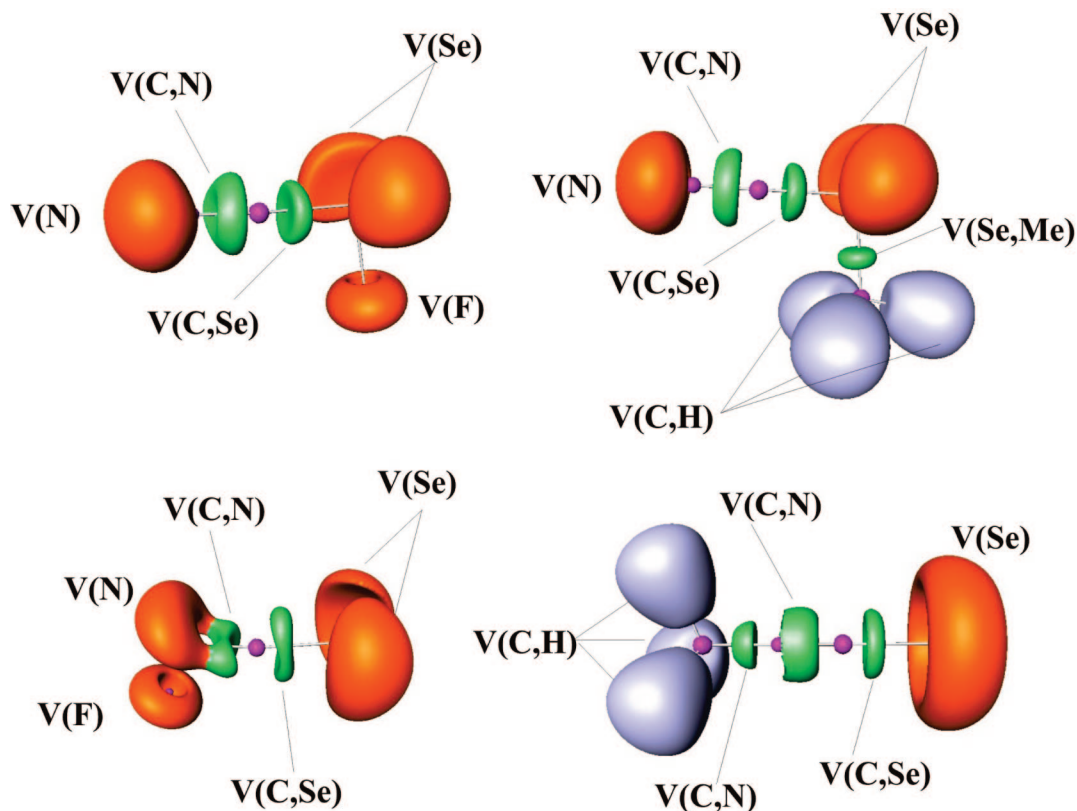


Figure 2. Three-dimensional representations of ELF isosurfaces with ELF = 0.80 for the F and Me derivatives of selenocyanates and isoselenocyanates. Blue lobes correspond to V(C,H) basins, orange lobes correspond to V(N), V(Se), and V(F) basins associated with N, Se, and F lone-pairs. Green lobes correspond to V(C,Se) and V(C,N) basins.

with the halogen atom electronegativity as testified by the V(Se,X) basin population. Coherently, the Wiberg bond orders for these linkages increase slightly on going from F to Br (0.73, 0.95, 0.98), whereas the electron density at the BCP decreases (0.141, 0.110, 0.099 au, respectively) as a consequence of the size increase of the substituent. The same behavior is observed for the delocalization indexes (0.96, 1.16, 1.22). The constancy along the series of the characteristics of the CN and CSe bonds are also mirrored in the constant values of the electron densities at the BCPs, which for the CSe bond vary from 0.173 to 0.171, whereas for the CN bond, it is constant and equal to 0.457. For these bonds, the delocalization indexes also remain nearly constant, ~ 1.18 for CSe and ~ 2.34 for CN.

There are significant changes on going from the selenocyanates to the corresponding isoselenocyanates. The first important change affects to the CSe bond, for which two connected disynaptic basins, pointing to a certain C=Se double bond character (see Figure 2) are located with a population about $1 e^-$ greater than for the selenocyanate isomers. The delocalization indexes, close to 2.0, are consistent with this interpretation.

The population of the V(C,N) disynaptic basins, as well as the CN delocalization index, also clearly decreases. Both changes point to a significant participation of mesomeric form **a** and, accordingly, to a parallel decrease of the participation of form **c**. A NRT analysis, actually shows that on going from the selenocyanate to the isoselenocyanate derivative, the weight of form **a** dramatically increases (from 11% to 61% for the F derivative and to 52% for the Cl and

Br derivatives). Concomitantly, the weight of the mesomeric form **c** decreases from 87% to 37% in the case of F derivative and to 46% in the case of the Cl and Br derivatives.

The aforementioned changes in the bonding patterns are reflected in both the electron densities at the BCPs and at the molecular force field. As a matter of fact, the electron density at the CN BCP decreases from 0.457 au in the selenocyanates to 0.411 au in the iso-derivatives. The electron density at the CSe BCP, which for the selenocyanates was 0.172 au, on average, becomes 0.197 au in average for the isoselenocyanates. As far as the stretching frequencies are concerned, while for selenocyanates the CN and CSe stretching modes appear at 2255 and 545 cm^{-1} , respectively, for the iso-derivatives, they appear in the regions of 1980 and 840 cm^{-1} , respectively, the latter being strongly coupled with the NX stretching mode.

Bonding changes are also significant for the Me derivative, but while for the halogen derivatives form **a** becomes dominant, for the Me derivative, form **c** still weights more than form **a**, even though their participation is rather similar (56% and 43%, respectively). This is consistent with the fact that, whereas in the methyl derivative the XNCSe skeleton is linear, for the halogen derivatives it is not and the XCN angle varies from 114.6° to 131.7° on going from the F- to the Br-substituted compound. Once more, the electron densities at the BCPs are in agreement with the previous discussion. The electron density at the CN BCP decreases by about 0.05 au, whereas that the CSe BCP increases by about 0.03 au.

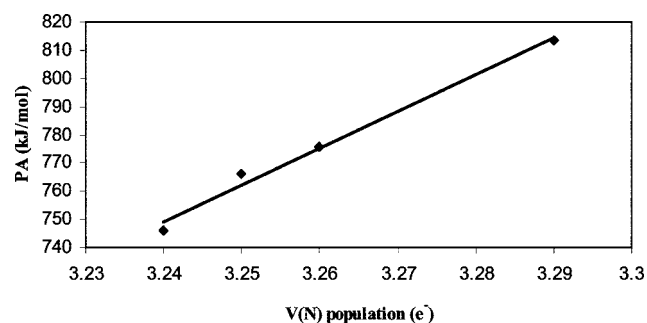
Table 3. Valence Basin Populations for N-Protonated Selenocyanates and Isoselenocyanates Derivatives

X	V(Se)	V(Se,X)	V(Se,C)	V(C,N)	V(N)	V(N,H)	V(X)
F	2 × 2.26		2.52	2.81		2.37	2 × 3.77
				2.25			
Cl	2 × 2.32	0.94	2.53	2.35		2.36	2 × 3.28
				2.74			
Br	2 × 2.33	0.99	2.54	2.29		2.35	6.76
				2.82			
CH ₃	2 × 2.30	1.35	2.59	2.15		2.33	
				2.98			

X	V(Se)	V(N,X)	V(Se,C)	V(C,N)	V(N)	V(N,H)	V(X)
F	2 × 2.37	0.66	1.81	1.33	0.76	2.09	2 × 2.22
			1.88	1.33	0.76		2.25
Cl	2 × 2.42	1.12	1.78	1.30	0.77	2.06	2 × 2.63
			1.87	1.30	0.77		2 × 0.53
Br	2 × 2.44	1.12	1.73	1.32	0.80	2.02	2 × 2.02
			1.87	1.32	0.80		2.54
CH ₃	2 × 2.47	1.63	1.76	1.36	0.59	2.04	
			1.81	1.36	0.59		

Bonding Analysis of the Protonated Compounds. The valence basin populations of the N-protonated selenocyanates and isoselenocyanates are summarized in Table 3.

It can be observed that N protonation leaves the number of basins of selenocyanate derivatives unchanged because a density transfer toward V(C,N) is possible since the SeC bond has mostly a single bond character. Hence, following the prescription of the “least topological change”,⁶⁷ the protonation occurs in the most populated basin provided the number of basins remains constant, in agreement with the fact the N-protonation is strongly favored with respect to X- or Se-protonation. Interestingly, there is also a rather good linear correlation between the calculated proton affinities and the population of the V(N) basin, which is the one directly involved in the protonation process (see Figure 3). The same correlation cannot be established for the isoselenocyanate derivatives because the number of basins is not preserved. In this series, the number of basins is increased by 2. As CSe has a strong double bond character, a charge of about 1 e⁻ from V(N) would make the carbon hyper-valent, therefore the opposite transfer (i.e., toward V(N)) is observed and the former V(N) basin gives rise to one V(N,H) basin and two symmetrically disposed V(N) basins. The trigonal bipyramid arrangement of the basins around the N center is consistent with Gillespie’s VSEPR rules.

**Figure 3.** Linear correlation between the calculated proton affinity (PA) and the population of the V(N) basin for selenocyanate derivatives.

It is also apparent that N-protonation triggers a certain electron density reorganization, through a slightly larger participation of mesomeric form **a**, leading to an increase of the population of the V(C,Se) basin. In fact, the weight of this form, according to the NRT analysis, increases up to 16% and the BO of the CSe bond becomes 1.21. Quite interestingly, also for the isoselenocyanates there is a reinforcement of the CSe bond upon N-protonation, but even stronger than that observed for the selenocyanate analogues. This is nicely illustrated by the increase in both the population of the V(C,Se) basin, from about 3.1 e⁻ to 3.7 e⁻, on average, and the electron density at the BCP (from 0.19 to 0.21 au), which therefore results in a significant increase of the Wiberg BO, which for the neutral species was around 2.0 and for the N-protonated ones becomes typically around 2.4. Simultaneously, the CN bond loses part of its double bond character (its BO being only 1.48). This dramatic increase in the CSe BO and in the population of the V(C,Se) basin points to a significant participation of mesomeric form **d** (see Scheme 1), which is indeed confirmed by a NRT analysis, which shows this form to become dominant (52%): the second dominant one (43%) is form **a**.

Relationship between Stability and Bonding. One question remains still to be answered, why are the selenocyanates halogen derivatives more stable, in general, than the corresponding iso-analogues, whereas for the methyl substituent, it is the other way around? As we have mentioned above, the characteristics of the CN and CSe bonds within each family of isomers are rather constant when the substituents are halogens but differ significantly when the substituent is a methyl group. One of the most striking differences is that on going from the selenocyanates to the iso-derivatives, the CN linkage becomes significantly weaker for the halogen derivatives, but not much for the methyl derivative. As a matter of fact, the ELF of the methyl-isoselenocyanate (see Figure 2) clearly shows a cylindrical symmetry of the CN basin, compatible with a dominant triple bond character, whereas for the F derivative, two connected basins are found in this region, which are consistent with a double bond character. The electron density at the CN BCP also reflects this difference, being larger (0.420 au) for the Me derivative than for the F derivative (0.410 au). This change would imply a larger destabilization of the system on going from the selenocyanate isomer to the iso-analogue when the substituent is F than when the substituent is Me. To this, some other important differences in the characteristics of the Se–X and N–X bonds are to be added. As shown in Figure 2, the Se–Me bond has a clear covalent character, whereas the Se–X bond, when X is a halogen atom, is strongly ionic in character, as reflected by the absence of valence basins in the Se–X region. The rather large polarizability of Se renders this interaction very strong. The important consequence is that the Se–X (X = F, Cl, Br) bonds are stronger than the Se–Me bond. As a matter of fact, the calculated Se–F bond dissociation energy, for instance, is 59 kJ mol⁻¹ greater than the Se–Me bond dissociation energy. On the other hand the N–Me bond in the iso-derivatives is significantly stronger than the N–X (X = F, Cl, Br) as clearly illustrated by the populations of the corresponding V(N,X) basins. This is not

surprising if one takes into account the fact that the N–X bond involves two very electronegative atoms when X is a halogen, and as was the case in the F₂ molecule, the bond is weak because electron density accumulates preferentially in the vicinity of both atoms rather than in the internuclear region.⁶⁸ This is clearly confirmed by the N–X dissociation energies in the isoselenocyanates derivatives. For example, the N–Me bond dissociation energy is 149 kJ mol^{–1} greater than the N–F bond dissociation energy.

Conclusions

According to our analysis of the bonding in selenocyanates and isoselenocyanates derivatives in terms of ELF, AIM, and NBO approaches, there are three main factors which explain why the former are more stable than the latter when the substituents are halogens, whereas for alkyl substituents, it is the other way around: (a) the Se–X (X = F, Cl, Br) bonds are much stronger than the Se–X (X = Me) bonds; (b) the N–X (X = F, Cl, Br) bonds are much weaker than the N–X bonds (X = Me) ones; (c) on going from the selenocyanates to the iso-selenocyanates, there is a significant weakening of the CN bond, which becomes essentially a double bond, when the substituents are halogen atoms, whereas upon methyl substitution the CN bond retains its triple bond character.

The same stability trends are observed for the corresponding N-protonated species. More importantly, the calculated stability differences are rather similar to those obtained for the neutral compounds, with the only exception of the methyl derivative. The obvious consequence is that selenocyanates and isoselenocyanates exhibit rather similar basicities in the gas-phase. Only for the methyl derivative, the latter isomer is 21 kJ mol^{–1} more basic than the former. Both types of isomers behave as nitrogen bases in the gas phase.

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Supporting Information Available: B3LYP/6–311+G(3df,2p) total energies and thermal corrections to the enthalpy and entropies for selenocyanates, iso-selenocyanates, and their nitrogen protonated species. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Norbury, A. H. *Adv. Inorg. Chem. Radiochem.* **1965**, 17, 231.
- (2) Patai, S., Ed. *the Chemistry of Cyanates and Their Thio Derivatives*; Wiley: New York, 1977; Vol. Parts 1 and 2.
- (3) Weaver, W. E.; Whaley, W. M. *J. Am. Chem. Soc.* **1946**, 68, 2115.
- (4) Franklin, W. J.; Werner, R. L.; Ashby, R. A. *Spectrochim. Acta* **1974**, A-30, 387.
- (5) Arase, A.; Masuda, Y. *Chem. Lett.* **1976**, 1115.
- (6) Tamura, Y.; Adachi, M.; Kawasaki, T.; Kita, Y. *Tetrahedron Lett.* **1979**, 2251.
- (7) Franklin, W. J.; Werner, R. L. *Tetrahedron Lett.* **1965**, 3003.
- (8) Franklin, W. J.; Werner, R. L.; Ashby, R. A. *Spectrochim. Acta* **1974**, A 30, 1293.
- (9) Huang, Y.; Chen, R. Y. *Synth. Commun.* **2000**, 30, 377.
- (10) Sommen, G. L.; Linden, A.; Heimgartner, H. *Eur. J. Org. Chem.* **2005**, 3128.
- (11) Gerbaux, P.; Dechamps, N.; Flammang, R.; Reddy, P. N.; Srinivas, R. *Rapid Commun. Mass Spectrom.* **2006**, 20, 151.
- (12) Richards, R. J.; Davis, R. W.; Gerry, M. C. L. *J. Chem. Soc., Chem. Commun.* **1980**, 915.
- (13) Frost, D. C.; Macdonald, C. B.; McDowell, C. A.; Westwood, N. P. C. *J. Am. Chem. Soc.* **1981**, 103, 4423.
- (14) Jonkers, G.; Grabandt, O.; Mooyman, R.; Delange, C. A. *J. Electron Spectr.* **1982**, 26, 147.
- (15) Leung, H.; Suffolk, R. J.; Watts, J. D. *Chem. Phys.* **1986**, 109, 289.
- (16) Jonkers, G.; Mooyman, R.; Delange, C. A. *Mol. Phys.* **1981**, 43, 655.
- (17) Li, Y. M.; Qiao, Z. M.; Sun, Q.; Zhao, J. C.; Li, H. Y.; Wang, D. X. *Inorg. Chem.* **2003**, 42, 8446.
- (18) Medarde, M.; Lopez, J. L.; Morillo, M. A.; Tome, F.; Adeva, M.; Sanfeliciano, A. *Tetrahedron Lett.* **1995**, 36, 8097.
- (19) González, A. I.; Mó, O.; Yáñez, M. *J. Phys. Chem. A* **1999**, 103, 1662.
- (20) Panda, A.; Mughesh, G.; Singh, H. B.; Butcher, R. J. *Organometallics* **1999**, 18, 1986.
- (21) Krief, A.; Delmotte, C.; Colaux-Castillo, C. *Pure Appl. Chem.* **2000**, 72, 1709.
- (22) Nguyen, T. M.; Lee, D. *Org. Lett.* **2001**, 3, 3161.
- (23) Braverman, S.; Zafrani, Y.; Gottlieb, H. E. *Tetrahedron* **2001**, 57, 9177.
- (24) Kennedy, R. A.; Mayhew, C. A. *Phys. Chem. Chem. Phys.* **2001**, 3, 5511.
- (25) Sanz, P.; Mó, O.; Yáñez, M. *Chem.—Eur. J.* **2002**, 8, 3999.
- (26) Nguyen, T. M.; Guzei, I. A.; Lee, D. *J. Org. Chem.* **2002**, 67, 6553.
- (27) Uehlin, L.; Fragale, G.; Wirth, T. *Chem.—Eur. J.* **2002**, 8, 1125.
- (28) Thompson, K. C.; Canosa-Mas, C. E.; Wayne, R. P. *Phys. Chem. Chem. Phys.* **2002**, 4, 4133.
- (29) Sanz, P.; Mó, O.; Yáñez, M. *New* **2002**, 26, 1747.
- (30) Graiff, C.; Predieri, G.; Tiripicchio, A. *Eur. J. Inorg. Chem.* **2003**, 1659.
- (31) Musaev, D. G.; Geletii, Y. V.; Hill, C. L.; Hirao, K. *J. Am. Chem. Soc.* **2003**, 125, 3877.
- (32) Bachrach, S. M.; Demoin, D. W.; Luk, M.; Miller, J. V. *J. Phys. Chem. A* **2004**, 108, 4040.
- (33) Poleschner, H.; Seppelt, K. *Chem.—Eur. J.* **2004**, 10, 6565.
- (34) Bajor, G.; Veszpremi, T.; Riague, E. H.; Guillemin, J. C. *Chem.—Eur. J.* **2004**, 10, 3649.
- (35) Cardey, B.; Enescu, M. *ChemPhysChem* **2005**, 6, 1175.

- (36) Tuononen, H. M.; Suontamo, R.; Valkonen, J.; Laitinen, R. S.; Chivers, T. *J. Phys. Chem. A* **2005**, *109*, 6309.
- (37) Guillemin, J. C.; Riague, E. H.; Gal, J. F.; Maria, P. C.; Mó, O.; Yáñez, M. *Chem.—Eur. J.* **2005**, *11*, 2145.
- (38) Bleiholder, C.; Werz, D. B.; Koppel, H.; Gleiter, R. *J. Am. Chem. Soc.* **2006**, *128*, 2666.
- (39) Iwamoto, T.; Sato, K.; Ishida, S.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **2006**, *128*, 16914.
- (40) Dutton, J. L.; Tuononen, H. M.; Jennings, M. C.; Ragogna, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 12624.
- (41) Coles, M. P. *Curr. Org. Chem.* **2006**, *10*, 1993.
- (42) Anderson, J. S. M.; Ayers, P. W. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2371.
- (43) Berski, S.; Gajewski, G.; Latajka, Z. *J. Mol. Struct.* **2007**, *844*, 278.
- (44) Pearson, J. K.; Boyd, R. J. *J. Phys. Chem. A* **2007**, *111*, 3152.
- (45) Salon, J.; Sheng, J.; Jiang, J. S.; Chen, G. X.; Caton-Williams, J.; Huang, Z. *J. Am. Chem. Soc.* **2007**, *129*, 4862.
- (46) Shishkina, S. V.; Shishkin, O. V.; Desenko, S. M.; Leszczynski, J. *J. Phys. Chem. A* **2007**, *111*, 2368.
- (47) Kaur, D.; Sharma, P.; Bharatam, P. V.; Kaur, M. *Int. J. Quantum Chem.* **2008**, *108*, 983.
- (48) Pearson, J. K.; Boyd, R. J. *J. Phys. Chem. A* **2008**, *112*, 1013.
- (49) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.
- (50) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (51) Pearson, J. K.; Ban, F. Q.; Boyd, R. J. *J. Phys. Chem. A* **2005**, *109*, 10373.
- (52) Trujillo, C.; Mó, O.; Yáñez, M.; Tortajada, J.; Salpin, J.-Y. *J. Phys. Chem. B* **2008**, *112*, 5479.
- (53) Trujillo, C.; Mó, O.; Yáñez, M. *ChemPhysChem*, **2008**, [Online] DOI: 10.1002/cphc.200800215.
- (54) Becke, A. D.; Edgecombe, K. E. *J. Chem. Phys.* **1990**, *92*, 5397.
- (55) Silvi, B.; Savin, A. *Nature* **1994**, *371*, 683.
- (56) Savin, A.; Becke, A. D.; Flad, J.; Nesper, R.; Preuss, H.; Vonscherner, H. G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 409.
- (57) Silvi, B. *J. Phys. Chem. A* **2003**, *107*, 3081.
- (58) Kohout, M.; Pernal, K.; Wagner, F. R.; Grin, Y. *Theor. Chem. Acc.* **2004**, *112*, 453.
- (59) Silvi, B. *Phys. Chem. Chem. Phys.* **2004**, *6*, 256.
- (60) Noury, S.; Krokidis, X.; Fuster, F.; Silvi, B. *Comput. Chem.* **1999**, *23*, 597.
- (61) *Amira 3.0* Template Graphics Software Inc.: San Diego, CA, 2002.
- (62) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Clarendon Press: Oxford, U.K., 1990.
- (63) Fradera, X.; Austen, M. A.; Bader, R. F. W. *J. Phys. Chem. A* **1999**, *103*, 304.
- (64) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985.
- (65) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
- (66) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. *NBO-5.0*; Theoretical Chemistry Institute, University of Wisconsin: Madison, WI, 2004; <http://www.chem.wisc.edu/~nbo5> (accessed March 23, 2008).
- (67) Fuster, F.; Silvi, B. *Chem. Phys.* **2000**, *252*, 279.
- (68) Cremer, D.; Kraka, E. *Angew. Chem., Int. Ed. Engl.* **1984**, *96*, 612.

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