A Gas-Phase Basicity Scale for Selenocarbonyl Compounds Based on High-Level *ab Initio* and Density Functional Theory Calculations

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A basicity scale for selenocarbonyl derivatives which covers a wide range of values (60 kcal/mol) has been established through the use of high-level *ab initio* and DFT calculations. In our theoretical survey we have included selenoformaldehyde and the corresponding BH_2, CH_3, NH_2, F, and Cl mono- and disubstituted derivatives, as well as carbonyl selenide, thiocarbonyl selenide, and selenoketene. With the only exception of selenoketene, which is a carbon base, all selenocarbonyl compounds investigated behave as selenium bases in the gas phase. Selenocarbonyl derivatives are predicted to be equally or slightly more basic than the thiocarbonyl analogues and, therefore, more basic than the corresponding carbonyl compounds. We have also shown, by means of G2-type calculations, that substituent effects on the relative stability of the neutral and the protonated forms of selenocarbonyl series are also rather similar to those estimated, at the same level of theory, for the thiocarbonyl series. For the neutrals these substituent effects are always stabilizing. Protonated species are strongly stabilized by σ- and π-electron donors, while they are destabilized by σ-withdrawing substituents. This explain the enhanced basicity of the methyl and amino derivatives and the low intrinsic basicity of the halogen derivatives. For the thiocarbonyl series the G2 calculated proton affinities are in very good agreement with the experimental values, which allow us to be confident in our estimates regarding the proton affinities of the selenocarbonyl derivatives investigated. The B3LYP/6-311+G(3df,2p) estimated proton affinities are slightly higher than the G2 values. The keto−enol isomerization of the methyl, hydroxy, and amino monosubstituted derivatives has been also studied.

Introduction

In the last decade a great deal of effort was devoted to the study of gas-phase reactions between organic and inorganic systems with different ions.[1] In this way it was possible to establish the so-called *intrinsic reactivity,* i.e., the reactivity of the isolated system without interference of possible solute−solvent interactions. In our group we have been interested in the reactivity of organic bases containing multiple bonds. Particular attention was devoted to the series of carbonyl[2] and thiocarbonyl[3] derivatives in an effort to establish the analogies and differences between both series of compounds, in particular as far as their protonation in the gas phase is concerned.

Unfortunately, experimental data on these functional groups are not abundant.[4] The primary reason seems to be the instability of compounds containing multiple bonds between elements of the second and subsequent rows of the periodic table.[5] In general, these species polymerize very easily, and therefore, the study of the monomers is only feasible at very low pressures in the gas phase or in noble-gas or nitrogen matrices.[6]

It is then not surprising to find that very little information, both experimental and theoretical, is available for selenocarbonyl compounds.[4] In particular, the lack of information about their intrinsic reactivity is almost complete. The aim of this paper is to partially alleviate this situation by undertaking a systematic study, through the use of high-level *ab initio* and density functional theory calculations, on the structures, harmonic vibrational frequencies, and gas-phase proton affinities of a series of selenocarbonyl compounds, including different kinds of substituents. For this purpose we have considered a wide set of monosubstituted and disubstituted derivatives of selenoformaldehyde, $H_2C{=}Se$, as well as OCSe, SCSe, and selenoketene, $H_2C{=}C{=}Se$. Some of the derivatives considered have been synthesized or detected, while some others have never been obtained, but they have been included in our survey for the sake of completeness and to have good models to understand the nature of the substituent effects on the different properties of the system.

Computational Details

To ensure some reliability of our estimates of the gas-phase proton affinities of the selenocarbonyl derivatives included in this study, we used the G2 theory of Pople et al.[7] This is a composite procedure based on the 6-311G(d,p) basis set and several basis extensions, where electron correlation effects are treated at the MP4 and QCISD(T) levels of theory. The final energies are effectively at the QCISD(T)/6-311+G(3df,2p) level, assuming that basis set effects on the correlation energies are additive. A small empirical correction (HLC) to accommodate remaining deficiencies is finally added as well as the corresponding zero point energy (ZPE) correction, estimated at the HF/6-31G* level. The reader is addressed to ref 7 for a complete description of this method. Recently, Curtiss et al.[8] reported basis set expansions for some third row elements which allow one to extent this high-level *ab initio* theory to selenium-containing compounds. Also recently an assessment of the G2 theory for the computation of enthalpies of formation has been published.[9] Since it has been shown that in some cases the QCISD(T) procedure exhibits a pathological behaviors,[10] we have investigated whether the use of a CCSD(T) formalism instead of the QCISD(T) one, within the G2 procedure, has some

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influence on our estimated proton affinities. These test calculations have been carried out for the set of monosubstituted derivatives of selenoformaldehyde.

Since the theoretical studies on selenium-containing systems are rather scarce[11−13] and most of them were limited to the use of small basis set expansions at the HF and MP2 levels of theory, we have considered it also of interest to investigate the performance of density functional theory to adequately describe these kinds of systems. Among the different functionals currently available we have chosen the B3LYP method, which has been shown to perform reasonably well when describing compounds containing other third row elements as As.[14] The B3LYP approach is a hybrid method which includes the Becke's three-parameter nonlocal exchange potential[15] with the nonlocal correlation functional of Lee, Yang, and Parr.[16] For the sake of consistency, the geometries of the different selenocarbonyl derivatives and their protonated species were fully optimized using the 6-31G* basis set, which is the expansion normally used for the geometry optimizations within the G2 theory. The harmonic vibrational frequencies were obtained at the same level, and the corresponding zero point energy (ZPE) corrections were scaled by the empirical factor 0.96, recently proposed by Curtiss et al.[17] The final energies were evaluated in single point calculations using the 6-311+G(3df,2p) basis set, which is the largest expansion used in the G2 theory. Recently, Altmann et al.[18] have found that the B3P86 approach, where the correlation part of the functional is provided by Perdew's 1986 expansion,[19] gives better results for sulfur bonds than other hybrid functionals. Therefore we have investigated if this is also true when dealing with selenium-containing compounds. For this purpose we have chosen the set of monosubstituted derivatives of the selenoformaldehyde. The corresponding geometries were optimized at the B3P86/6-31G* level, and the final energies were obtained in single-point calculations using a 6-311+G(3df,2p) basis set expansion. All these calculations have been carried out using the Gaussian-94 series of programs.[20]

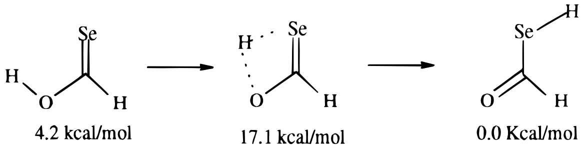
To investigate the bonding characteristics of the different species, we used the natural bond orbital (NBO) analysis of Weinhold et al.[21] and the atoms in molecules (AIM) theory of Bader.[22] The first formalism provides values for the atomic natural total charges and describes the bonding in terms of the natural hybrids centered on each atom. Using the second approach we have located the bond critical points, i.e., points where the electron density function, $\rho(\mathbf{r})$, is minimum along the bond path and maximum in the other two directions. The values of the charge at these critical points is a good measure of the strength of the linkage. The AIM analysis was performed using the AIMPAC series of programs.[23] All these population analyses have been carried out at the B3LYP/6-31G* level.

Results and Discussion

Geometries. The total energies of the different selenocarbonyl compounds and their corresponding protonated species are given in Table 1. The MP2/6-31G* as well as the B3LYP/6-31G* optimized geometries are given as Supporting Information. Most of the species investigated present several conformers, but only the geometry and the energy of the most stable one, both for neutral and for protonated species, are reported.

The experimental information on the structures of selenocarbonyl compounds is very scarce, and we are only aware of that of selenoformaldehyde,[24] selenocarbonyl difluoride,[25] and selenoketene,[26] while a partially resolved structure was reported[27] for selenoacetaldehyde. The corresponding structural parameters are compared with our theoretical estimates in Table 2. It can be seen that the agreement between calculated and experimental values is very good. It can be also observed that, in general, the bond lengths obtained at the B3LYP/6-31G* level are longer than those obtained at the MP2 level but in better agreement with the experimental values. In general, the B3P86 approach yields C=Se bond distances 0.01 A shorter than the B3LYP ones and, therefore, in worse agreement with the available experimental values. Consistently, the B3LYP-calculated rotational constants for selenoformaldehyde (A = 293.977 GHz, B = 12.465 GHz, C = 11.958 GHz) are in better agreement with the experimental ones[28] (A = 290.528 GHz, B = 12.454 GHz, C = 11.918 GHz) than the B3P86 ones (A = 293.506 GHz, B = 12.585 GHz, C = 12.068 GHz).

SCHEME 1



Our MP2/6-31G*-optimized geometry for selenourea does not differ significantly from the MP2/3-21G*-optimized geometry reported by Ha and Puebla[11] for the *transoid* conformer, the largest differences (0.005 Å) affecting the C−N bond lengths. However, in contrast with the conclusions of these authors, we have found that the *cissoid* conformer is not a stationary point of the potential energy surface (PES), since it collapses without activation barrier to the planar conformer. The planar conformer is found to be a transition state connecting the two enantiomers of the *transoid* conformer of the selenourea, rather than connecting the *transoid* and the *cissoid* conformers, since its sole imaginary frequency corresponds to the out-of-phase combination of the wagging displacement of both amino groups.

Initially we had included in our theoretical survey also the hydroxy (X=OH) selenocarbonyl derivative. In this kind of derivatives a possible enolization of the C=Se function cannot be discarded, so we have also estimated the relative stability of the corresponding selenolic isomer: HSeHC=O, which was found to be 4.2 kcal/mol more stable than the corresponding selenocarbonyl (HOHC=Se) at the G2 level of theory. We have considered it also of interest to estimate the activation barrier associated with this isomerization process. The corresponding transition state is estimated to lie 17.1 kcal/mol above the selenocarbonyl isomer and 21.3 kcal/mol above the selenolic form (See Scheme 1), so one must reasonably expect that the selenolic form must be clearly dominant in the gas phase. Therefore in what follows we will not discuss the intrinsic basicity of the hydroxy derivatives. In view of these results we have considered it necessary to investigate also the relative stability of the enolic forms when the substituent is a methyl or an amino group. In these two cases however, the selenolic forms, H_2C=CHSeH and HN=CHSeH, are found to be 2.3 and 9.7 kcal/mol less stable, respectively, than the corresponding selenocarbonyl forms.

Although a detailed description of the optimized geometries of the different derivatives and their protonated forms is not the main goal of this paper, some general trends should be noted. In all compounds the C=Se bond length varies within narrow limits (1.693−1.814 Å). Carbonyl and thiocarbonyl analogs exhibit a similar behavior. In general, as it was also found for carbonyl[35] and thiocarbonyl[3a] compounds, σ-electron-withdrawing substituents, as F or Cl, lead to a shortening of the C=Se bond, while σ-electron donor groups, as CH_3 and BH_2, lead to

TABLE 1: Total Energies *E* (hartrees), Unscaled Zero-Point Energies *E*(ZPE) (hartrees), and Proton Affinities PA (kcal/mol) of the XYC═Se and XYC═S Species at the Different Levels of Theory Used in This Study with Values in Italics Corresponding to the Protonated Forms

		total energies				proton affinities			
		selenocarbonyls			thiocarbonyls	selenocarbonyls		thiocarbonyls	
X	Y	*E*(B3LYP) [*E*(ZPE)]	*E*(G2)[a]	*E*(G2/MP2)	*E*(G2)	PA (B3LYP)[b]	PA(G2)[c] [PA(G2/MP2)]	PA (G2)	PA (exp)[d]
H	H	−2440.838 00 [0.024 17]	−2439.173 27 (−2439.172 92)	−2439.168 14	−436.933 70	185.8	184.8 [185.5]	183.8	185.0
		−2441.140 82 [0.033 67]	*−2439.465 35 (−2439.464 94)*	*−2439.461 35*	*−437.224 22*				
H	BH_2	−2466.288 23 [0.035 91]	−2464.543 36	−2464.537 64		186.9	185.3 [185.9]		
		−2466.596 211 [0.044 05]	*−2464.836 36*	*−2464.831 50*					
H	CH_3	−2480.176 04 [0.053 22]	−2478.406 80 (−2478.40635)	−2478.400 54	−476.168 27	196.6	193.7 [194.4]	193.5	
		−2480.495 38 [0.061 89]	*−2478.71311 (−2494.712 54)*	*−2478.707 88*	*−476.474 29*				
H	NH_2	−2496.250 01 [0.043 22]	−2494.472 26 (−2494.471 51)	−2494.465 03	−492.233 69	205.7[e]	205.0 [205.8][e]	204.8	
		−2496.584 74 [0.052 85][e]	*−2494.796 62*[a] *(−2494.795 98)*	*−2494.790 61*[e]	*−492.557 74*	181.4[f]	186.7 [187.61][f]		
		−2496.550 91 [0.056 36][f]	*−2494.767 63*[f]	*−2494.761 75*[f]					
H	F	−2540.120 27 [0.017 85]	−2538.334 83 (−2538.333 87)	−2538.326 69	−536.099 37	177.7	175.9 [176.7]	178.1	
		−2540.409 70 [0.026 82]	*−2538.612 82 (−2538.611 79)*	*−2538.605 93*	*−536.372 88*				
H	Cl	−2900.471 95 [0.016 30]	−2898.329 16	−2898.315 78	−896.091 38	185.1	183.0 [183.9]	181.1	
		−2900.774 206[0.025 32]	*−2898.618 43*	*−2898.606 27*	*−896.377 58*				
CH_3	CH_3	−2519.510 84 [0.081 48]	−2517.640 77	−2517.633 48	−515.402 85	204.7	200.9 [201.5]	201.2	
		−2519.842 39 [0.089 52]	*−2517.958 54*	*−2517.952 25*	*−515.721 21*				
NH_2	NH_2	−2551.646 44 [0.060 84]	−2549.764 16	−2549.755 05	−547.525 01	215.4[e]	214.0 [214.8][e]	214.0	213.8
		−2551.996 01 [0.069 91][e]	*−2550.102 80*[e]	*−2550.094 97*[e]	*−547.863 67*	191.5[f]	192.4 [193.0][f]		
		−2551.961 59 [0.073 68][f]	*−2550.068 34*[f]	*−2550.060 24*[f]					
F	F	−2639.402 62 [0.010 64]	−2637.499 19	−2637.487 76	−635.264 11	173.4	171.7 [172.6]	167.7	
		−2639.685 11 [0.019 56]	*−2637.770 47*	*−2637.760 46*	*−635.528 96*				
Cl	Cl	−3360.098 24 [0.007 25]	−3357.479 73	−3357.459 61	−1355.242 41	185.8	183.3 [184.1]	180.7	180.7
		−3360.400 44 [0.015 99]	*−3357.769 46*	*−3357.749 00*	*−1355.528 04*				
O		−2514.939 47 [0.008 63]	−2513.183 63	−2513.176 68		155.5[g]	156.6 [157.4]		
		−2515.191 66 [0.015 66][g]	*−2513.430 89*[g]	*−2513.425 06*[g]		146.7[h]	147.8 [148.7]		
		−2515.180 10 [0.018 25][h]	*−2513.416 81*[h]	*−2513.411 27*[h]					
S		−2837.890 85 [0.006 33]	−2835.768 25	−2835.757 67		167.3[i]	167.9 [169.0][i]		
		−2837.161 78 [0.013 35][i]	*−2836.033 49*[i]	*−2836.024 65*[i]		164.5[j]	165.7 [166.7]		
		−2837.157 98 [0.013 98][j]	*−2836.029 94*[j]	*−2836.020 97*[j]					
CH_2		−2478.939 88 [0.029 09]	−2477.192 71	−2477.186 96		180.8[k]	179.7 [180.3][k]		
		−2479.234 63 [0.037 75][k]	*−2477.476 74*[k]	*−2477.471 87*[k]		198.9[l]	202.5 [203.4][l]		
		−2479.267 10 [0.041 73][l]	*−2477.512 97*[l]	*−2477.508 73*[l]					

[a] Values within parentheses correspond to the use of a CCSD(T) formalism instead of the QCISD(T) one within the G2 procedure. [b] The PAs (in kcal/mol) using B3P86 functional are the following: X = H, Y = H → PA = 187.0; X = H, Y = CH_3 → PA = 197.0; X = H, Y = NH_2 → PA = 205.9; X = H, Y = F → PA = 178.1. [c] The PAs (in kcal/mol) using a CCSD(T) formalism in the G2 procedure are the following X = H, Y = H → PA = 184.7; X = H, Y = CH_3 → PA = 193.6; X = H, Y = NH_2 → PA = 205.0; X = H, Y = F → PA = 175.8. [d]Experimental values taken from ref 3a. [e] Protonation at Se. [f] Protonation at N. [g] Protonation at Se. [h] Protonation at O. [i] Protonation at Se. [j] Protonation at S. [k] Protonation at Se. [l] Protonation at CH_2.

TABLE 2. Geometries of Selenocarbonyl Compounds XYC═Se

	X = Y = H				X = CH_3, Y = H				X = Y = F			H_2C═C═Se		
	MP2	B3LYP	B3P86	exp[a]	MP2	B3LYP	B3P86	exp[b]	MP2	B3LYP	exp[c]	MP2	B3LYP	exp[d]
C═Se	1.724	1.748	1.739	1.753	1.753	1.757	1.749	1.75	1.732	1.744	1.743	1.692	1.697	1.706
C−X	1.076	1.090	1.089	1.090	1.492	1.492	1.485		1.283	1.316	1.314	1.314[e]	1.308[e]	1.303[e]
C−Y	1.076	1.090	1.089	1.090	1.092	1.093	1.093		1.283	1.316	1.314	1.086[f]	1.087[f]	1.091[f]
XCSe	122.0	122.1	122.0	121.0	125.6	126.2	126.0	125.7	126.1	126.2	126.2	120.6[g]	120.9[g]	120.1[g]
YCSe	122.0	122.1	122.0	121.0	118.7	118.9	118.9		126.1	126.2	126.2			

[a] Values taken from ref 24. [b] Values taken from ref 27. [c] Values taken from ref 25. [d] Values taken from ref 26. [e] C═C bond length. [f] C−H bond length. [g] CCH bond angle.

a lengthening of the C═Se linkage. Although the BH_2 group behaves also as a π-electron acceptor, the σ-electron donor effect dominates. For amino substituents, which behave simultaneously as σ-electron-withdrawing and π-electron donors, the latter effect clearly dominates due to the favorable conjugation of the amino lone pair with the C═Se π-system, and the C═Se linkage significantly lengthens.

These substituent effects are well reflected in the characteristics of the C−Se bonding molecular orbitals. As illustrated in Table 3, in the a-bonding MO the s character of the carbon hybrid increases when the substituents are σ-electron withdrawing. As expected, this effect is maximum when both substituents are fluorine atoms. On the contrary, when the substituent is a σ-electron donor, as the methyl group or the BH_2 group, the s character of the carbon hybrids, slightly decreases. For the π-bonding orbital, it is apparent that substituents which behave as π-electron acceptors, as the BH_2 group, or as strong π-electron donors, as the amino group, induce a significant decrease in the participation of the carbon hybrids. It can be also observed that the methyl group behaves as a π-electron donor through a typical hyperconjugative effect and that the π-donor character of the fluorine atoms is enhanced in the disubstituted derivative. Consistently the C═Se bond is slightly longer and the charge density at the bcp slightly smaller ($\rho_c = 0.187$ au) in the F_2C═Se species than in the corresponding monosubstituted FHC═Se derivative ($\rho_c = 0.195$ au).

TABLE 3: NBO Population analysis of the σ and π C−Se bonds[a]

		C−Se σ bond		C−Se π bond	
X	Y	C	Se	C	Se
H	H	59(35s + 65p)	41(17s + 82p)	45(100p)	55(100p)
H	BH_2	56(26s + 74p)	44(13s + 86p)	37(100p)	62(100p)
H	CH_3	60(34s + 66p)	40(17s + 82p)	43(100p)	57(100p)
H	NH_2	62(37s + 63p)	38(15s + 84p)	34(100p)	66(100p)
H	F	60(40s + 59p)	40(16s + 83p)	41(100p)	59(100p)
CH_3	CH_3	61(32s + 68p)	39(17s + 82p)	41(100p)	59(100p)
NH_2	NH_2	62(38s + 62p)	37(14s + 85p)	26(100p)	74(100p)
F	F	61(48s + 52p)	39(14s + 85p)	38(100p)	62(99p)

[a] For each bond the participation of each atomic hybrid is given. The s and p character of each hybrid orbital is indicated within parenthesis.

It is also worth mentioning that the shortest C═Se bond lengths correspond to those systems, as O═C═Se, S═C═Se and $H_2C{=}C{=}Se$, where the selenocarbonyl carbon presents a sp hybridization pattern. Consistently, the charge density at the corresponding bcp (ρ_c = 0.202 au) is higher than for the remaining selenocarbonyl compounds.

Upon protonation at the Se heteroatom there is, on average, a 0.04 Å elongation of the C═Se linkages, which indicates that selenium behaves as slightly more electronegative than carbon.[29] This elongation of the C−Se linkage upon protonation is particularly large for the mono- and disubstituted fluorine derivatives. Simultaneously, the XCY bond angle opens due to the rehybridization undergone by the carbonyl carbon atom. Protonation causes a considerable polarization of the C═Se bonding charge toward the heteroatom, which results in an increase of the p character of the hybrid involved in this bond. By orthogonality, the hybrids involved in the C−X and the C−Y bonds should increase their s character leading to a concomitant increase of the angle between them.

We have also estimated the relative stability of the protonated species formed by protonation at the substituent when its heteroatom is endowed with lone pairs and therefore is a potential basic site. For both the mono- and the disubstituted amino derivatives, we have found that the forms protonated at the amino group are local minima of the PES, which lie 18.2 and 21.6 kcal/mol above the selenium protonated forms, respectively. For the monosubstituted compound protonation at the selenium atom yields two different conformers. The conformer in which the proton is *trans* with respect to the amino group is predicted to be slightly more stable (0.3 kcal/mol) than the *cis* conformer.

In both fluorine and chlorine monosubstituted compounds, the *cis* conformer of the selenium protonated species is estimated to be slightly more stable than the *trans* one as a consequence of the stabilizing nonbonding interaction between the proton attached to selenium and the halogen atom. Protonation at the halogen atom leads to a C−X bond fission, yielding a hydrogen halide molecule and a $YC{=}Se^+$ cation as products of the protonation process. This phenomenon is due to the strong activation undergone by C−X bonds upon protonation, which was discussed in detail elsewhere.[30]

Protonation of carbonyl selenide and thiocarbonyl selenide, OCSe and SCSe, takes place also preferentially at the selenium atom, although for the latter the sulfur protonated species lies only 2.3 kcal/mol higher in energy than the selenium protonated structure. Protonation of selenoketene takes place however preferentially at the β carbon atom to yield the $CH_3{}^+CH{=}Se$ cation, while the selenium protonated form is estimated to be about 23 kcal/mol higher in energy.

Hence, we may conclude that all selenocarbonyls investigated, with the only exception of selenoketene, behave as selenium bases in the gas phase.

Harmonic Vibrational Frequencies. The experimental information on the vibrational spectra of selenocarbonyl compounds is rather scarce. At present the ground-state vibrational spectrum of selenoformaldehyde has not been observed, and only some ab initio data are available.[12] The vibrational frequencies of selenocarbonyl difluoride[31] and dichloride[32] have been measured in rare-gas matrices. The corresponding experimental frequencies are compared with the B3LYP/6-31G*-calculated ones in Table 4. In general the agreement between both sets of values is fairly good. On average the highest vibrational frequencies are overestimated by about 2−4%, while for the lowest ones the agreement is remarkably better. For the remaining species investigated the calculated harmonic vibrational frequencies are available from the authors upon request. Nevertheless, we have illustrated in Table 5 how the C═Se stretching frequency changes with the nature of the substituent. It can be observed that σ-withdrawing substituents shift it to higher frequency values, while σ-donor and π-donor substituents produce a significant red-shifting. The charge density at the corresponding bond critical points changes accordingly. In fact the AIM analysis shows that while the charge density at the C═Se bcp in selenoformaldehyde is 0.193 au, in the fluorine-substituted derivative the charge density becomes 0.195 au, and in the amino-substituted one the value decreases to 0.179 au. It is also evident that the aforementioned blue-shifting is, as expected, much smaller for chlorine- than for fluorine-substituted compounds. For S═C═Se and $H_2C{=}C{=}Se$, the C═Se and the C═X stretching displacements appear coupled as symmetric and asymmetric combinations.

For the different protonated species the Se−H harmonic stretching frequency varies within very narrow limits ($\Delta\nu$ = 50 cm^{-1}) in the region of 2400 cm^{-1}. In general, the values for the disubstituted derivatives appear slightly blue-shifted with respect to those the corresponding monosubstituted compounds. Also importantly, and in agreement with the charge density redistribution mentioned above, the C−Se stretching frequency in the protonated forms appears significantly red-shifted with respect to the neutral species. This effect is particularly strong

TABLE 4: Harmonic Vibrational Frequencies (in cm^{-1}) of $X_2C{=}Se$ Species Calculated at the B3LYP/6-31G(d) Level of Theory with Values Given Within Parentheses Corresponding to Experimental Ones[a]

X = H			X = F			X = Cl		
3211	b_2 [3059][b]	CH_2 asym stret	1321	a_1 (1287)	C−Se stret	1002	a_1 (991)	C−Se stret
3118	a_1 [2988]	CH_2 sym stret	1251	b_2 (1207)	CF_2 asym stret	784	b_2 (805)	CCl_2 asym stret
1492	a_1 [1397]	CH_2 bend	717	a_1 (705)	CF_2 sym stret	445	b_1 (-)	CCl_2 wagg
965	b_1 [942]	CH_2 wagg	592	b_1 (575)	CF_2 wagg	436	a_1 (437)	CCl_2 sym stret
924	b_2 [914]	CH_2 rock	434	a_1 (432)	CF_2 bend	265	a_1 (260)	CCl_2 bend
899	a_1 [874]	C−Se stret	352	b_2 (351)	CF_2 rock	252	b_2 (248)	CCl_2 rock

[a] Experimental values taken from refs 31 and 32. [b] Values within brackets are scaled *ab initio* values taken from ref 12.

TABLE 5: Stretching Frequency (in cm^{-1}) of the C=Se Bond of the XYC=Se Species

X	Y	ν (cm^{-1})	X	Y	ν (cm^{-1})
H	H	901	F	F	1321
BH_2	H	847	Cl	H	943
CH_3	H	743	Cl	Cl	1002
CH_3	CH_3	618	O		682
NH_2	H	735	S		1486 (asym), 530 (sym)
NH_2	NH_2	656	CH_2		1814 (asym), 700 (sym)
F	H	1372			

for the selenocarbonyl halides, which also experienced the largest lengthening of this bond upon protonation.

Gas-Phase Basicities. The calculated proton affinities of the selenocarbonyl compounds under investigation have been summarized in Table 1. These PA values correspond to the enthalpies of the gas-phase protonation reactions. Hence, they include the ZPE, the thermal, and the $P\Delta V$ corrections. Unfortunately there is an almost complete lack of experimental values to compare with. Actually, to the best of our knowledge, only the gas-phase basicities of selenoformaldehyde and carbonyl selenide have been reported so far.[33] The agreement between our G2 estimate and the experimental value is excellent for the former; but it is no so good for the latter, for which the theoretical value is 4.6 kcal/mol higher than the experimental one. Since in general, the agreement between G2 and experimental proton affinities is very good,[34] even for third-row bases,[14b] a reevaluation of the experimental value would be desirable.

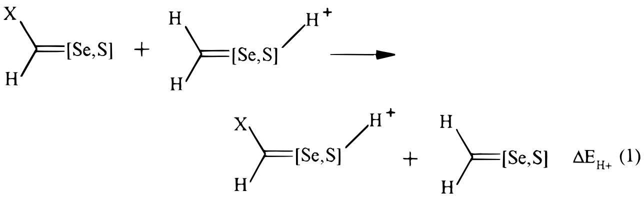
It can be also observed that the B3LYP/6-311+G(3df,2p) proton affinities are systematically greater than the G2 ones, with the only exceptions being those of carbonyl and thiocarbonyl selenides. These differences are usually smaller than 2.0 kcal/mol, although for the case of the mono- and dimethyl derivatives the differences are particularly large (2.9 and 3.8 kcal/mol, respectively). The agreement between G2 estimates and DFT values is slightly worse when the B3P86 functional is used (see Table 1). Also interestingly, the differences between G2 and G2(MP2) estimates are always lower than 1 kcal/mol. This means that the latter formalism is a good alternative which implies a nonnegligible computational effort saving. Finally, it can be also observed that the use of a CCSD(T) formalism instead of the QCISD(T) one has a negligibly small effect (0.1 kcal/mol or smaller) on the calculated proton affinities (see Table 1).

TABLE 6: Calculated energies (Δ*E*, kcal/mol) for the Isodesmics Reactions 1−3

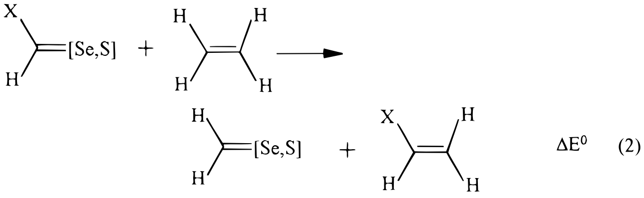
		$\Delta E°$ (reacn 2)		ΔE^+ (reacn 3)		ΔE_{H^+} (reacn 1)	
X	Y	C=Se	C=S	C=Se	C=S	C=Se	C=S
H	H	0.0	0.0	0.0	0.0	0.0	0.0
CH_3	H	+2.7	+3.4	+11.6	+13.1	+8.9	+9.7
NH_2	H	+14.8	+15.5	+35.1	+36.5	+21.0	+21.0
F	H	+3.4	+5.9	−5.5	−4.7	−8.9	−10.7
Cl	H	+2.2	+3.3	+0.5	+0.6	−1.8	−2.7
CH_3	CH_3	+2.2	+3.3	+0.5	+0.6	−1.8	−2.7
NH_2	NH_2	+10.4	+10.0	+19.3	+19.2	+90	+9.2
F	F	+5.1	+5.3	+0.9	−0.1	−4.2	−5.4
Cl	Cl	−1.1	−0.8	−0.8	−1.2	+0.3	−0.3

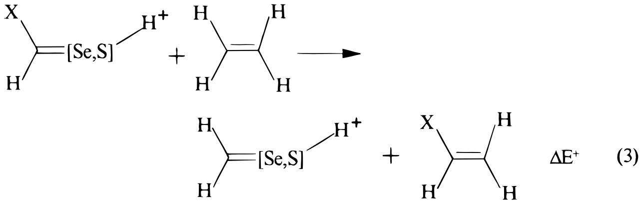
The calculated proton affinities cover a wide range (about 60 kcal/mol) of the basicity scale, which place in evidence important substituent effects on the intrinsic basicity of the selenocarbonyl function. Analogous behaviors were reported before for similar sets of carbonyl[35] and thiocarbonyl[3a] derivatives. Since no experimental values are currently available for the proton affinities of selenocarbonyl systems to be compared with those of the thiocarbonyl or carbonyl analogs, we have decided to carry out such a comparison in terms of the G2 estimated values. For this purpose we have also evaluated the proton affinities of the thiocarbonyl derivatives which include CH_3, NH_2, F, and Cl as substituents. For the sake of completeness we have considered both the mono- and disubstituted derivatives. The corresponding values have been summarized in Table 1. The first conspicuous feature is the very good agreement between the G2 calculated values and the experimental ones[3a] when available. The second important feature to be noted is the rather small differences between the intrinsic basicity of selenocarbonyl and the thiocarbonyl analogs. In fact, the selenocarbonyl compounds are predicted to be only slightly more basic than the corresponding thiocarbonyl derivatives. These differences are typically smaller than 1 kcal/mol, with the exception of the halogen derivatives for which these differences increase up to 4 kcal/mol, for the particular case of the selenocarbonyl difluoride.

This seems to indicate that very likely the substituent effects on the relative stability of selenocarbonyl compounds and their protonated forms do not differ significantly from those found for the corresponding thiocarbonyl derivatives. To analyze this problem from a more quantitative point of view we will use the same kind of isodesmic reactions employed in ref 3a.



This isodesmic reaction may be decomposed into two reactions accounting respectively for substituent effects on the neutral and on the protonated forms:





Obviously, reaction 1 can be obtained by simply adding to eq 2 the opposite of eq 3. As it was previously found for carbonyl[35] and thiocarbonyl[3a] compounds, reaction 2 is predicted to be always endothermic (see Table 6), with the only exception of the dichloride derivative, for which it is slightly exothermic. This means that all substituents lead to a stabilization of the selenocarbonyl group. More importantly, in quantitative terms, this stabilization effect is equal or slightly smaller than that estimated for the corresponding thiocarbonyl analogs (see Table 6).

For methyl and amino substituents reaction 3 is significantly more endothermic than reaction 2. Hence, similarly to what has been found for other bases as pyridines[36] and azoles,[37] sub-

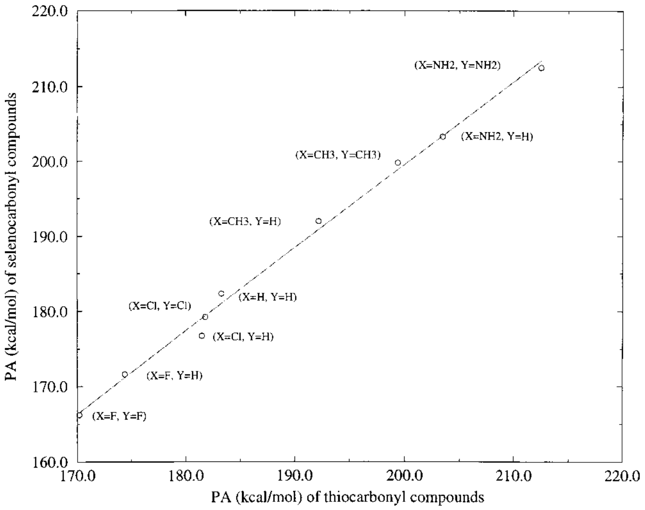


Figure 1. Linear correlation between the proton affinities (PA) of selenocarbonyl and thiocarbonyl derivatives. Values are estimated at the G2 level of theory. The linear regression fulfills the equation PA(Se) = 1.11PA(S) − 22.3 kcal/mol ($r = 0.997$).

stituent effects are clearly dominant in the corresponding protonated species (see Table 6). Again, these stabilization effects are equal or slightly smaller than those estimated for the thiocarbonyl analogues, explaining the rather small differences between the intrinsic basicities of both series of compounds.

We can then conclude that it is the extra stabilization of the protonated molecule which is responsible for the enhanced basicity of the methyl- and amino-substituted derivatives. This is not the case, however, as far as the fluorine derivatives are concerned. In this case the neutral forms are only slightly stabilized, while the protonated species are clearly destabilized. Accordingly, these derivatives are less basic than the parent compound. In the fluorine derivatives the carbonyl carbon is an electron deficient atom, due to the high electronegativity of the substituents. In the protonated species, a considerable amount of charge is transferred from the basic center (S or Se) to the proton, and only if the substituents can be further polarized toward the carbonyl carbon will the system be stabilized. This is the case for BH_2, CH_3, or NH_2, but when the substituent is highly electronegative as fluorine, this polarization is not likely to occur. Chlorine is less electronegative and more polarizable than fluorine, and the protonated species are slightly stabilized for the monosubstituted derivative and slightly destabilized for the disubstituted compound. For BH_2 which behaves as a σ-donor and a π-acceptor, the stabilization of the selenocarbonyl function is rather small, for both neutral and protonated species. As a consequence, the BH_2 derivative is only slightly more basic than the parent compound.

The main conclusion is that substituent effects on the relative stabilities of neutral and protonated species of selenocarbonyl compounds and therefore on their intrinsic basicities are almost equal to those found for the thiocarbonyl analogs (see Figure 1). Taking into account that, as it has been shown by Abboud et al.,[3a] the differential substituent effects on the intrinsic basicities of thiocarbonyls are 20% smaller than in the carbonyl series, we may conclude that also for selenocarbonyl derivatives the differential substituent effects are 20% smaller than in the carbonyl series, although both thiocarbonyl and selenocarbonyl compounds are consistently more basic than their carbonyl analogs.

Similar effects have been analyzed for the corresponding disubstituted compounds. In these cases the values of ΔE° and ΔE^+ are referred to the corresponding monosubstituted derivative. The values reported in Table 6 clearly indicate that both for thiocarbonyl and selenocarbonyl derivatives there is a certain attenuation of the substituent effect on the intrinsic basicity of the system. This attenuation is particularly significant when the substituent is an amino group, while it is much smaller when the substituent is a methyl group.

TABLE 7. Estimated Heats of Formation (Δ_fH) of XHC=Se Monosubstituted Selenocarbonyl Derivatives at the G2 Level of Theory with All Values in kcal/mol

compd	Δ_fH	compd	Δ_fH
$CH_3CH{=}Se$	27.6 (27)[a]	$FCH{=}Se$	−11.1
$NH_2CH{=}Se$	17.7	$ClCH{=}Se$	28.3

[a] Experimental value taken from ref 38.

The strong analogy between the substituent effects in the thiocarbonyls and the selenocarbonyls indicates that both series of compounds should exhibit an almost identical molecular orbital distribution, which as discussed in ref 3a is different from that expected for the carbonyl derivatives.

Heats of Formation. The isodesmic reaction 2 may alternatively be used to estimate the heat of formation of monosubstituted selenocarbonyl derivatives, provided that the experimental heats of formation of the remaining compounds intervening in reaction 2 are known. This is the case[38] for the selenoformaldehyde and for the $XCH{=}CH_2$ vinyl derivatives when X = CH_3, NH_2, F, and Cl and therefore, we could estimate the heats of formation of the corresponding XHC=Se selenocarbonyl derivatives. The values obtained are given in Table 7. To the best of our knowledge only the experimental heat of formation of the methyl derivative is known and the agreement with our estimate is fairly good, so we might be confident in the reliability of the remaining predicted values.

Conclusions

Through the use of high-level *ab initio* and DFT calculations we have established a basicity scale for selenocarbonyl derivatives which covers a wide range of values. With the only exception of selenoketene, which as its oxygen- and sulfur-containing analogs is a carbon base, all selenocarbonyl compounds investigated behave as selenium bases in the gas phase. Selenocarbonyl derivatives are predicted to be equally or slightly more basic than the thiocarbonyl analogues and, therefore, more basic than the corresponding carbonyl compounds. We have also shown that substituent effects on the relative stability of the neutral and the protonated forms of selenocarbonyl derivatives are also rather similar to those estimated, at the same level of theory, for the thiocarbonyl analogs, and, therefore, smaller than those found for the corresponding carbonyl derivatives. For the neutrals these substituent effects are always stabilizing. The protonated species are strongly stabilized only when the susbtituents are σ- and/or π-electron donors, while σ-electron-withdrawing groups destabilize them. This explains the enhanced basicity of the methyl and amino derivatives and the low basicity of the halogen derivatives. Also importantly substituent effects are not additive.

The B3LYP density functional approach yields proton affinities for the series of compounds investigated slightly higher than the G2 ones, in particular for methyl-substituted compounds, although the B3LYP-optimized geometries are in closer agreement with the experimental ones than the MP2 geometries. The performance of the B3P86 method for selenium-containing compounds is not better than that of the B3LYP functional.

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Supporting Information Available: A table of Cartesian coordinates for the selenocarbonyl compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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