

FULL PAPER

Computational Investigations of the Chalcogen-Substituted Carboxylic Acids $RC(=O)XH$ and $RC(=X)OH$ and their Dimers $[RC(=O)XH]_2$ and $[RC(=X)OH]_2$ ($X = S, Se, Te$)

D. Allen Clabo, Jr., Hamilton D. Dickson, and Toby L. Nelson

Department of Chemistry and Physics, Francis Marion University, Florence, South Carolina 29501 USA.
Tel.: (843) 661-1457; Fax: (843) 661-1440. E-mail: dclabo@fmarion.edu

Received: 20 October 1999/ Accepted: 1 February 2000/ Published: 28 February 2000

Abstract Semiempirical and *ab initio* theoretical methods have been used to investigate molecular structures of the chalcogen-substituted carboxylic acid isomers $RC(=O)XH$ (chalcogenol acid) and $RC(=X)OH$ (chalcogenon acid). A recent experimental report suggests that the chalcogenon isomers, although less stable at room temperature, predominate at low temperature in polar solvents and that there is only a small barrier to isomerization between the isomers. Theoretical calculations have been used to locate minimum energy structures of chalcogen-substituted carboxylic acid isomers and to calculate energy differences between pairs of isomers. Carboxylic acids are well known to dimerize, especially in the gas phase and in non-polar solvents. We have, therefore, also calculated energies of dimerization of the chalcogen-substituted acids by optimizing the geometries of the symmetric dimers. We note that the PM3 level of theory is only qualitatively correct for sulfur- and selenium-containing species but fails even qualitatively for the tellurium-containing compounds. *Ab initio* results confirm the experimental observations and provide good estimates of both isomerization and dimerization energies. We conclude that for many functional groups with tautomers $RC(=X)YH$ and $RC(=Y)XH$, the more acidic tautomer is the one with the acid proton on the smaller, more electronegative atom, although in many cases this may not be the more stable tautomer.

Keywords *Ab initio*, Semiempirical, Density functional theory, Chalcogens, Carboxylic acid

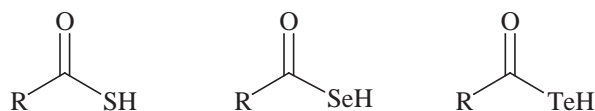
Introduction

One of the advantages of computational chemistry is the ability to examine any molecule or class of molecules, even

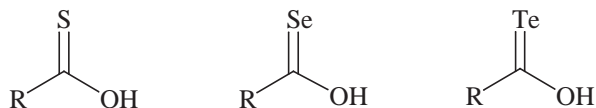
Correspondence to: D. A. Clabo

Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70th birthday

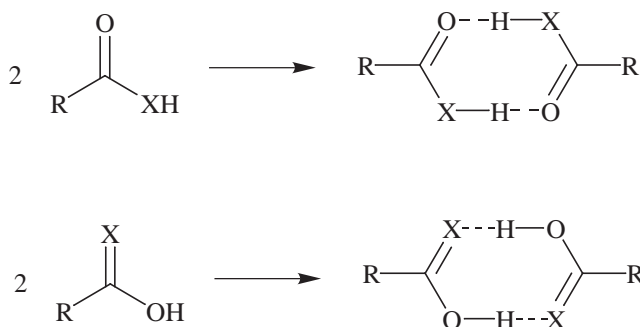
before it is completely characterized or understood experimentally. In cooperation with experiment, these computations can open new, previously unexplored areas of chemistry. In this regard, we were initially intrigued by the report of Kato and co-workers[1] on the relative stabilities of chalcogen-substituted carboxylic acid isomers. They noted that many thiocarboxylic acids (Scheme 1) have been well characterized and that several selenocarboxylic acids have recently been synthesized and characterized by their group.[2] Most important, however, in addition to observ-



Scheme 1 Chalcogenol acid tautomers of chalcogen-substituted carboxylic acids



Scheme 2 Chalcogenon acid tautomers of chalcogen-substituted carboxylic acids

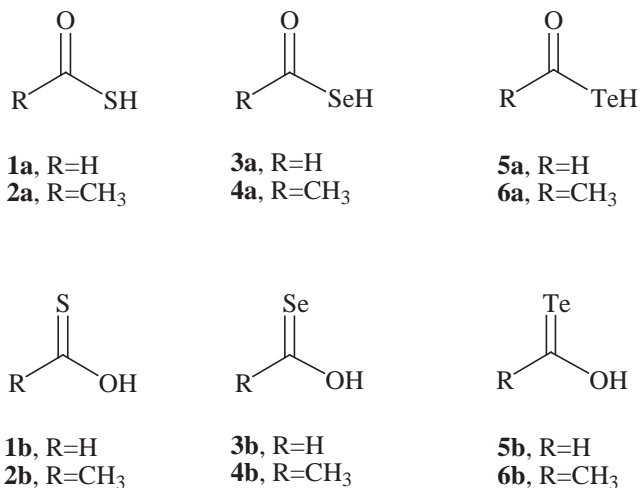


Scheme 3 Dimerization of chalcogenocarboxylic acids

ing the first tellurocarboxylic acids, they also reported that all of the chalcogen-substituted acids can be observed as their less stable tautomers (Scheme 2) in polar solvent at low temperature.[1,2]

We undertook this computational investigation to reconfirm the experimental findings of Kato and co-workers,[1,2] to provide new and additional computational data [3] on the structures and energies of small molecules in this new class of molecules that includes carbon-chalcogen multiple bonding, and to provide a theoretical basis for understanding and

predicting the relative energies of chalcogen-substituted carboxylic acid tautomers. In addition, theoretical calculations can determine the energetics of reactions, for example the energy of dimerization (Scheme 3) of these carboxylic acid analogues. These reaction energies may also provide insight into the character of the chalcogenocarboxylic acids and the experimental ease of interconversion of the tautomers. We report, therefore, dimerization energies for the simple chalcogenocarboxylic acids examined here.



Scheme 4 Chalcogenol and chalcogenon acid tautomers 1-6

Computational procedure

We report results from both semiempirical and *ab initio* computations. The semiempirical results have been obtained using the PM3 parameters for all atoms (H, C, O, S, Se, Te).[4] Molecular geometries of the molecules HC(=O)XH (**1a**, **3a**, **5a**), HC(=X)OH (**1b**, **3b**, **5b**), CH₃C(=O)XH (**2a**, **4a**, **6a**), and CH₃C(=X)OH (**2b**, **4b**, **6b**) (Scheme 4) were optimized and heats of formation were determined using the program

Scheme 5 Chalcogenol and chalcogenon acetic acid dimers 7-8

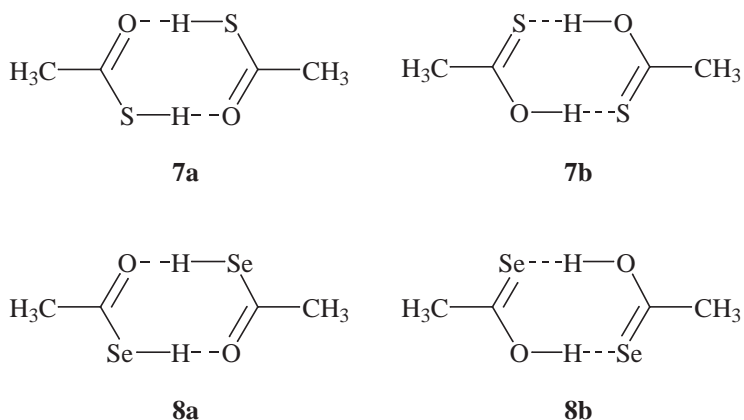


Table 1 PM3 enthalpies of formation (ΔH_f°) and relative energies ($\Delta\Delta H_f^\circ$) of $HC(=O)XH$, $HC(=X)OH$, $CH_3C(=O)XH$, and $CH_3C(=X)OH$ (kJ mol^{-1})

Isomer	ΔH_f°	Isomer	ΔH_f°	$\Delta\Delta H_f^\circ$
1a	-139.8	1b	-54.5	85.3
2a	-162.0	2b	-83.3	78.7
3a	-117.9	3b	-52.3	65.6
4a	-164.3	4b	-104.5	59.8

MOPAC as implemented in the graphical interface CAChe (Oxford Molecular, Ltd.) on a Windows 95-based desktop PC. Structures and heats of formation of the symmetric cyclic dimers **7a-8a** $\{[CH_3C(=O)XH]_2\}$ and **7b-8b** $\{[CH_3C(=X)OH]_2\}$ (Scheme 5) were first determined by repeated optimization at interfragment separation distances ($H\cdots O$ or $H\cdots X$) of 1 - 10 Å, then by full optimization including the interfragment distance. *Ab initio* results were obtained from density functional theory calculations using the GAUSSIAN98 suite of molecular electronic structure programs (Gaussian, Inc.) [5] on the Cray T-90 supercomputer at the San Diego Supercomputer Center. The hybrid density functional used was the three-parameter exchange functional of Becke [6] with the correlation functional of Lee, Yang, and Parr [7] (B3LYP), as implemented in GAUSSIAN98. Geometry optimizations were performed by analytical gradient methods [8] with the polarized split-valence 6-311+G** basis set [9]. All structures were characterized as minima and vibrational zero-point energies (ZPE) were determined by evaluation of the molecular Hessian (force constant) matrix obtained by analytical second derivative methods [10]. Final *ab initio* relative energies have been determined by addition

of unscaled B3LYP/6-311+G** ZPE differences to B3LYP/6-311+G** relative energies.

Results and discussion

Semiempirical results

RC(=O)SH and RC(=S)OH The standard state enthalpies of formation (ΔH_f°) of the thiol acid **1a** and thion acid **1b** (adopting the chalcogenol/chalcogenon terminology of Kato [1,2] to differentiate the isomers) are shown in Table 1. The known thiol acid **1a** is calculated to be more than 85 kJ mol^{-1} more stable than the thion isomer. This is in agreement with the general understanding [11] that thiocarboxylic acids under most conditions exist exclusively as the thiol tautomer. Figure 1 shows the PM3 optimized geometries of **1a** and **1b**, and the remaining geometrical parameters are given in Table 2. The geometry is in good agreement with the known structure of thioformic acid **1a**.

The enthalpies of formation of thiol **2a** (thioacetic acid) and its thion tautomer **2b** are shown in Table 1. Again, in agreement with experiment, the thiol tautomer is more stable, in this case by more than 78 kJ mol^{-1} according to the PM3 calculations. The optimized geometries of the thioacetic acid tautomers are shown in Figure 2. The geometries are unremarkable and the remaining geometrical parameters are listed in Table 2.

RC(=O)SeH and RC(=Se)OH The first test of the PM3 level of theory relative to the recent experimental data is in comparing selenol acid **3a** with the presumed less stable selenon acid **3b**. The calculated enthalpies of formation are shown in Table 1. In agreement with the observation that selenol acids

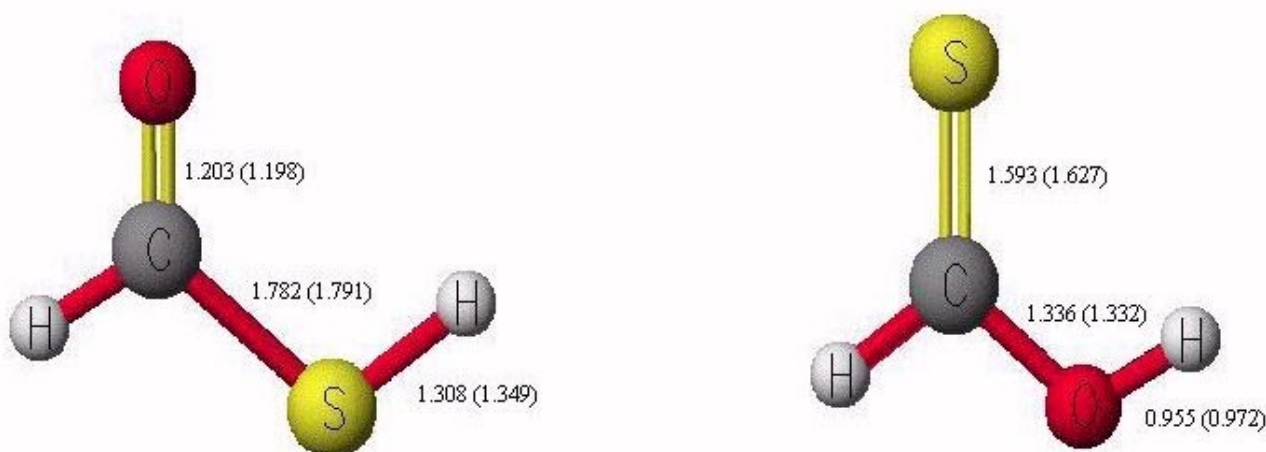


Figure 1 PM3 optimized geometries of $HC(=O)SH$ **1a** and $HC(=S)OH$ **1b**. B3LYP/6-311+G** optimized bond lengths are given in parentheses

Table 2 Selected PM3 optimized bond lengths (Å) and bond angles (°) for $RC(=X)YH$ molecules. Selected B3LYP/6-311+G** optimized parameters are given in parentheses

Species	r(C-H)	θ (OCX)	θ (CXH)	θ (HC=O)
	r(C-C)		θ (COH)	θ (HC=X)
				θ (CC=O)
				θ (CC=X)
1a	1.103 (1.105)	129.55 (125.92)	104.15 (95.00)	121.39 (123.69)
1b	1.104 (1.089)	129.94 (126.51)	110.30 (108.45)	126.02 (123.60)
2a	1.504 (1.513)	126.13 (122.61)	101.88 (94.56)	122.43 (123.90)
2b	1.499 (1.502)	126.70 (122.69)	109.41 (107.89)	124.20 (125.70)
3a	1.099 (1.105)	127.78 (125.75)	102.20 (93.27)	124.61 (123.96)
3b	1.096 (1.089)	126.75 (126.28)	109.86 (108.52)	126.42 (123.25)
4a	1.486 (1.513)	126.87 (122.33)	101.81 (92.90)	129.11 (124.29)
4b	1.477 (1.499)	126.26 (122.22)	108.40 (108.11)	121.16 (125.67)

are observed exclusively at room temperature,[1,2] the enthalpy of formation of the selenol tautomer **3a** is more than 65 kJ mol⁻¹ less than the selenon **3b**. The geometrical parameters are given in Table 2, and Figure 3 shows the PM3 optimized geometries of **3a** and **3b**.

The enthalpies of formation of the selenoacetic acids **4a** and **4b** are given in Table 1, and the geometries are tabulated

in Table 2 and displayed in Figure 4. Consistent with the theoretical predictions so far, the selenol tautomer **4a** is more stable at the PM3 level of theory by more than 59 kJ mol⁻¹ than the selenon isomer **4b**.

The difference in energy between the selenocarboxylic acid tautomers (65 and 59 kJ mol⁻¹) is somewhat less than for the thiocarboxylic acids (85 and 78 kJ mol⁻¹). This, too, is

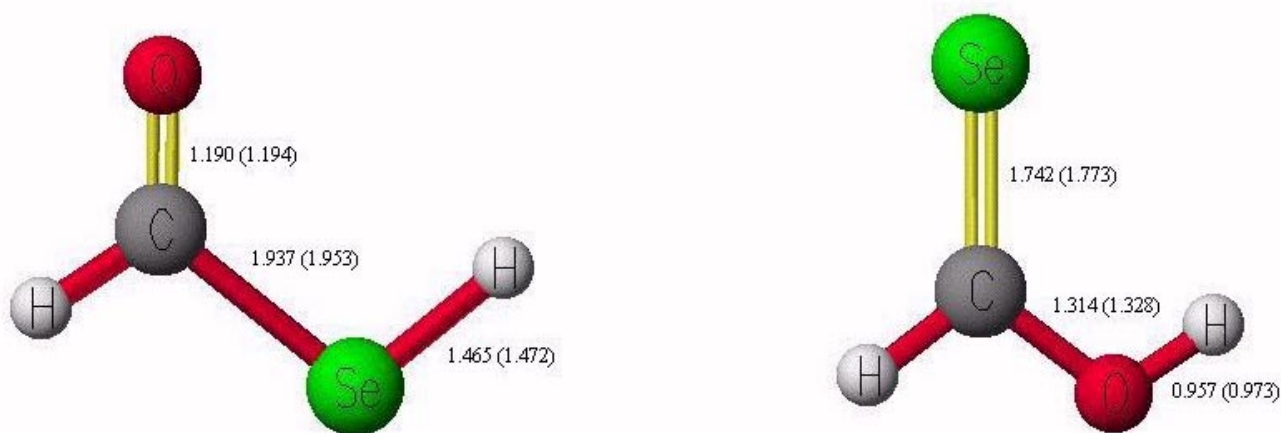
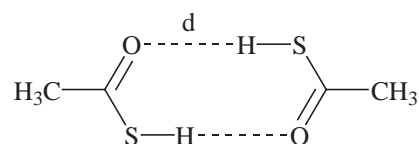


Figure 2 PM3 optimized geometries of $HC(=O)SeH$ **2a** and $HC(=Se)OH$ **2b**. B3LYP/6-311+G** optimized bond lengths are given in parentheses

qualitatively in accord with the experimental observations.[1,2] In particular, the fact that the tautomerization was first (and more readily) observed for the selenocarboxylic acids implies that the tautomers may lie slightly closer in energy. Note, however, that even the smallest energy difference between isomers (**4a** vs **4b**) corresponds to an equilibrium constant (**4b** \leftrightarrow **4a**) of more than 10^9 at 298 K. Thus, the PM3 predictions, although qualitatively in agreement with experiment, clearly fail to produce chemically reasonable relative energies.

RC(=O)TeH and RC(=Te)OH Using MOPAC as implemented in CAChe, PM3 optimization of the tellurium-containing carboxylic acid analogues failed to give reasonable structures (for example, Te-H bonds shorter than the atomic radius of Te). Whether this is the result of the MOPAC/CAChe implementation, of the PM3 parameters, or because of some other reason is not evident to us. Therefore, although we have attempted to characterize the tellurol and telluron acid tautomers **5a**, **5b**, **6a**, and **6b**, we have not obtained any meaningful results and, therefore, do not present any results here. These molecules (and the apparent difficulties of semiempirical theoretical calculations involving Te) are part of our continuing research into molecules with various chalcogen-containing functional groups.

[CH₃C(=O)SH]₂ and [CH₃C(=S)OH]₂ The enthalpy of dimerization is related directly to the hydrogen bonding and the acidity of a molecule. We have calculated the enthalpy of formation of the symmetric, cyclic dimers derived from the two tautomers of the thiocarboxylic acids at interfragment separation distances (*d*) from 1-10 Å (Scheme 6). The geometry was fully optimized at each successive fixed interfragment distance. Dimerization energies were first approximated from the well depth of the resulting graphs of ΔH_f° vs *d*. Beginning then with this graphical estimate of the optimum interfragment distance, the geometries of the dimers were fully optimized.



Scheme 6 Thiol acetic acid dimer showing interfragment distance *d*

The resulting enthalpies of dimerization are shown in Table 3. The thion acid **2b** forms a much stronger dimer (**7b**) than the thiol acid **2a** (dimer **7a**). This suggests that **2b**, although thermodynamically less stable in the gas phase (and, apparently also in the solid phase and in non-polar solvents[1]), is stabilized significantly by hydrogen bonding interactions. This self-association does not reverse the relative energies of the isomers since **7b** is still significantly less stable than **7a** at the PM3 level of theory. However, solvation could involve multiple solvent-solute hydrogen bonding interactions and the experimentally observed reversal of the tautomeric equilibrium in polar solvent is qualitatively suggested by our calculations.

In structural terms, these calculations suggest that the O-H bond of **2b** is a better hydrogen bond donor (to C=S) than the S-H bond of **2a** (to C=O). Further, one can conclude that **2b** is, therefore, also more acidic (that is, should more readily donate the acidic proton completely to a base acceptor). This conclusion is on first sight apparently not in agreement with the known acidities of the simple chalcogen acids. Because of increasing atomic size, increasing atomic polarizability, and decreasing bond strengths, H₂S is more acidic than H₂O and organic thiols (RSH) are more acidic than the analogous alcohols (ROH). That is, one would expect that the S-H bond of **2a** should be more acidic and the better hydrogen bond donor.

In contrast to the intrinsically more acidic S-H bond, thiol acid **2a** also has a strong C=O bond. When the S-H bond

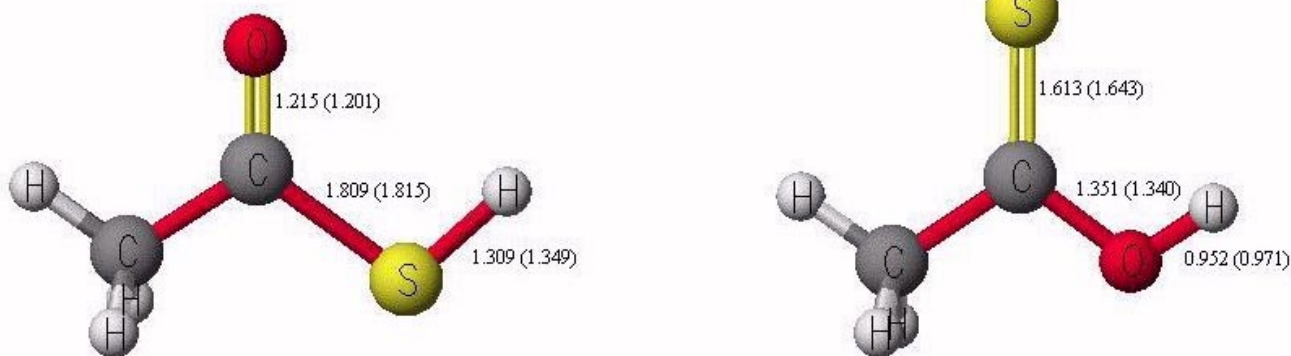


Figure 3 PM3 optimized geometries of CH₃C(=O)SH **3a** and CH₃C(=S)OH **3b**. B3LYP/6-311+G** optimized bond lengths are given in parentheses

Table 3 PM3 enthalpies of dimerization ($\Delta\Delta H_f^\circ = \Delta H_f^\circ(\text{dimer}) - 2*\Delta H_f^\circ(\text{monomer})$) for $[\text{CH}_3\text{C}(=\text{O})\text{XH}]_2$ and $[\text{CH}_3\text{C}(=\text{X})\text{OH}]_2$ molecules

Isomer	$\Delta\Delta H_f^\circ$ (kJ mol ⁻¹)
7a	-2.2 [a]
7b	-45.2
8a	-3.8 [b]
8b	-87.2

[a] Determined graphically ($\Delta H_f^\circ(\text{dimer})$ vs d) since full optimization gave **7b**

[b] Determined graphically ($\Delta H_f^\circ(\text{dimer})$ vs d) since full optimization gave **8b**

cleaves to form the conjugate base anion (CH_3COS^-), resonance increases electron density at the weaker C=S bond while depleting electron density from the stronger C=O bond. This net transfer of π -bonding from oxygen to sulfur is unfavorable and destabilizing and will lead to reduced acidity of the thiol acid **2a**. On the other hand, cleavage of the O-H bond in **2b**, although it is intrinsically less favored, forms the same conjugate base anion (CH_3COS^-). However, in forming the anion from **2b**, the C=S bond order is reduced and the C=O bond order is increased. Since the C=O bond is stronger than the C=S bond,[12,13] anion formation is more favorable for **2b**. The thion acid (**2b**) is consequently a better proton donor than the thiol acid (**2a**), not on the basis of the intrinsic acidity of the O-H or S-H bonds, but rather because of the difference in C=O vs C=S bond strengths.[12,13]

$[\text{CH}_3\text{C}(=\text{O})\text{SeH}]_2$ and $[\text{CH}_3\text{C}(=\text{Se})\text{OH}]_2$ The same explanations and conclusions apply in comparing selenol acid dimer **8a** with selenon acid dimer **8b**. The dimerization enthalpies of these two species are shown in Table 3. In this case, the selenon acid dimer **8b** has a much stronger hydrogen bond interaction (32 kJ mol⁻¹) than the corresponding selenol acid dimer (3.8 kJ mol⁻¹). Furthermore, **8b** is actually more stable than **8a** at the PM3 level. Not only is the intermolecular attraction stronger for **4b** than for **4a**, the thermodynamic preference after self-association is actually in favor of the selenon acid **4b**, the less stable selenocarboxylic acid monomer! This calculation clearly supports the experimental data. Not only can the selenon acid be experimentally observed more readily than the thion acid, but also the selenon acid exists in a higher proportion than the thion acid in equilibrium at the same temperature.[1,2] That is, the stabilization of the selenon acid is significantly greater than the corresponding thion acid.

The higher dimerization enthalpy for the selenon acid compared to the selenol acid can be explained with reasons analogous to those for the thion vs thiol acid dimers. That is, the intrinsically less acidic O-H bond of **4b** is cleaved preferentially because of the resulting increase of C=O bond character and associated decrease in C=Se bond character in the conjugate base. The fact that the C=Se bond is even weaker

than the C=S bond compared to the C=O bond leads to the greater difference in dimerization energies from the thiocarboxylic acids to the selenocarboxylic acids. We conclude that, in general for tautomers of the form $\text{RC}(=\text{X})\text{YH}$ and $\text{RC}(=\text{Y})\text{XH}$, the more acidic tautomer is the one with the acid proton on the smaller, more electronegative atom, although in many cases this may not be the more stable tautomer. Note that this generalization includes and is true for the case of many other functional groups, including organic keto-enol tautomers ($\text{X} = \text{O}$ and $\text{Y} = \text{CH}_2$) where the ketone is typically the thermodynamically more stable isomer but the acidity of a carbonyl-containing molecule is the result of the enol tautomer.

Ab initio results

We have continued our theoretical investigations by using *ab initio* density functional theory (DFT) methods to examine both tautomers of molecules **1** – **4**. These calculations, at a much higher level of theory than the semiempirical PM3 calculations already reported here, provide definitive predictions of the structures and relative energies of the isomeric chalcogenocarboxylic acids. Whereas the PM3 parameterization may or may not give accurate descriptions of this unusual class of molecules (see our comments above relative to the tellurium-containing molecules, for example), the *ab initio* DFT approach gives results that are more directly and confidently comparable to experiment. Thus, we are able not only to re-verify the experimental data with the *ab initio* calculations but also to judge our own semiempirical results.

HC(=O)SH and HC(=S)OH The total and relative energies of **1a** and **1b** are given in Table 4. Relative energies are expected to be well reproduced at the B3LYP/6-311+G** level of theory. Thus, the thiol acid **1a** is more stable, as expected, than its thion tautomer **1b**. The energy difference of only 18.8 kJ mol⁻¹ is much more chemically reasonable (than the difference obtained by PM3 calculations, *vide supra*) since both isomers have been observed. Optimization of the molecular geometries at the B3LYP/6-311+G** level of theory is also expected to give good agreement with experimental structural data. These optimized geometries are shown in Table 2 and in Figure 1. Although there are clearly differences between these values and those determined by PM3 (also in Table 2), these differences are, for the most part, the differences expected by improving the level of theory in any case. The only gross difference in geometry from PM3 to DFT in this case is with the bond angle at sulfur (θ (C-S-H)), where PM3 predicts 104.2°, hardly different from an exact tetrahedral angle, whereas DFT predicts 95.0°, much closer to the expectation based on structures of many organic thiols and sulfides, for example.

HC(=O)SeH and HC(=Se)OH Likewise, the total and relative energies of molecules **3a** and **3b** are given in Table 4, and the optimized geometries are shown in Table 2 and in Figure 2. Again, the expected selenol acid tautomer **3a** is

Table 4 Total, zero-point, and relative (in parentheses) energies of $RC(=O)XH$ and $RC(=X)OH$ molecules [a]

Species	B3LYP/6-311+G**[b]	ZPE[b]
1a	-512.7794437 (0.00)	72.97 (0.00)
1b	-512.7760706 (8.86)	82.93 (18.82)
2a	-552.1159916 (0.00)	145.94 (0.00)
2b	-552.1103709 (14.76)	155.48 (24.30)
3a	-2516.1083174 (0.00)	68.16 (0.00)
3b	-2516.1035639 (12.48)	81.00 (25.32)
4a	-2555.4451697 (0.00)	141.21 (0.00)
4b	-2555.4377221 (19.55)	153.47 (31.81)

[a] Total energies in a.u.; relative and zero-point energies in kJ mol^{-1}

[b] //B3LYP/6-311+G**

more stable than selenon acid **3b**, here by 25.3 kJ mol^{-1} . The larger energy difference between selenocarboxylic acid tautomers and the corresponding thiocarboxylic acid tautomers is a result of the larger difference in the strengths of C=Se and C=O bonds compared to C=S and C=O bonds. This reinforces the qualitative conclusion from the PM3 calculations about the relationship between the relative acidities of tautomeric chalcogenocarboxylic acids and the relative C=X (vs C=O) bond strengths. There are also no sur-

prises with respect to the optimized geometries of these isomers. As with the sulfur-containing species **1a** and **1b**, the only gross discrepancy from the PM3 results to the DFT results in Table 2 is the unrealistic bond angle at selenium (θ (C-Se-H)), where the DFT result of 93.3° is in close agreement with the value expected based on organic selenols and selenides.

$\text{CH}_3\text{C}(=\text{O})\text{SH}$ and $\text{CH}_3\text{C}(=\text{S})\text{OH}$ Extending our *ab initio* calculations to the stable, well studied thioacetic acid **2a** and its thion tautomer **2b**, the total, relative, and zero-point energies are presented in Table 4. As expected, the thiol tautomer **2a**, known to be the correct molecular structure for this molecule[14] is more stable than its thion tautomer **2b**. The energy difference of 24.3 kJ mol^{-1} is only slightly more than the 18.8 kJ mol^{-1} difference in thioformic acid tautomers **1a** and **1b**. The DFT optimized molecular parameters are shown as part of Figure 3 and are also tabulated in Table 2. As with the tautomers **1a** and **1b**, the changes in geometry from the semi-empirical to the DFT levels of theory are not dramatic. The exception again is the H-S-C angle, for which the DFT calculation provides a more accurate prediction of 94.6° , whereas the PM3 prediction of 101.9° is obviously incorrect.

$\text{CH}_3\text{C}(=\text{O})\text{SeH}$ and $\text{CH}_3\text{C}(=\text{Se})\text{OH}$ Finally, the absolute, relative, and zero-point energies of molecules **4a** and **4b** are listed in Table 4. These tautomers complete the *ab initio* investigation of the chalcogen-substituted carboxylic acid tautomers. These molecules, too, complete a consistent picture of the chalcogenocarboxylic acids, for which the chalcogenol tautomer is more stable. Here, selenol **4a** is more stable by 31.8 kJ mol^{-1} than selenon tautomer **4b**. The optimized molecular parameters of these molecules are included in Figure 4 and Table 2. As before, the geometries are unremarkable except to note that the bond angle at Se is incorrectly predicted by PM3 (101.8°), but more accurately described (92.9°) by the DFT calculations.

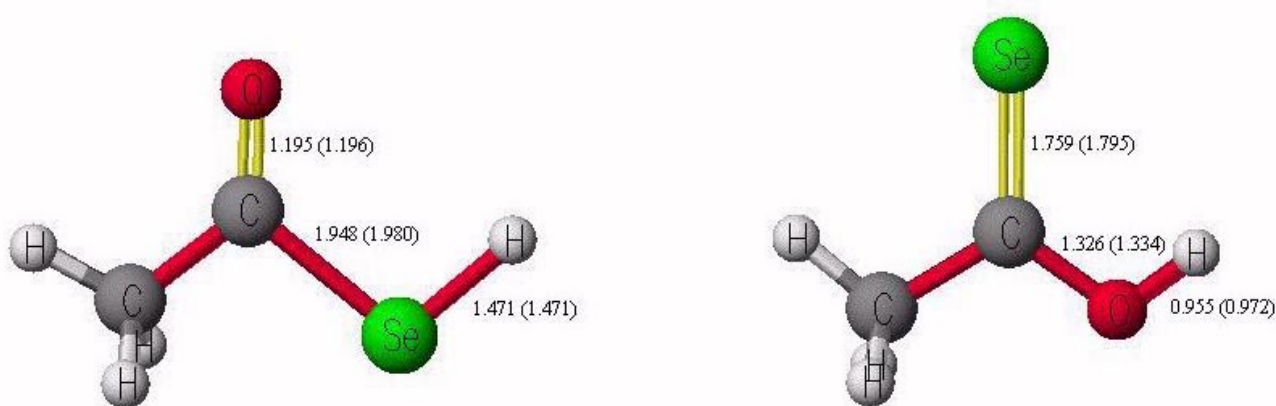


Figure 4 PM3 optimized geometries of $\text{CH}_3\text{C}(=\text{O})\text{SeH}$ **4a** and $\text{CH}_3\text{C}(=\text{Se})\text{OH}$ **4b**. B3LYP/6-311+G** optimized bond lengths are given in parentheses

The results of our research suggest that the PM3 level of theory is capable at best of only qualitatively reproducing most of the important structural features of the chalcogen-substituted carboxylic acids. Not unexpectedly, the energies predicted by PM3 grossly overestimate the differences between isomers. We have not addressed whether the relative enthalpies of dimerizations and relative energies of the dimers themselves are well estimated at the PM3 level of theory. The *ab initio* calculation of the structures and energies of dimers (**7** and **8**, for example) and of larger molecules, the determination of the structures and energies of tellurocarboxylic acid tautomers, and other points remain a part of our continuing investigations.

Conclusions

We have investigated the structures and energies of a series of chalcogen-substituted carboxylic acids. This new class of molecules demonstrates rather unusual carbon-to-chalcogen multiple bonding. In addition, a tautomeric form of the molecules has been observed experimentally and the equilibrium between tautomers demonstrated for these chalcogen-substituted carboxylic acids.[1,2] Our computational investigations have included optimizing the molecular geometries for sulfur- and selenium-containing isomers **1a**, **1b**, **2a**, **2b**, **3a**, **3b**, **4a**, and **4b** at the semiempirical PM3 and the B3LYP/6-311+G** density functional levels of theory. Our results confirm the observed relative stabilities of the chalcogenocarboxylic acid tautomers. The PM3 results clearly overestimate the isomeric energy differences. The geometries of the acid tautomers are qualitatively similar at both levels of theory, with the exception of the bond angles at the chalcogen (θ (C-X-H)) that are incorrectly predicted by PM3 in every case. Further, we have demonstrated that the less stable tautomer has the larger dimerization energy in every case examined. This is consistent with the experimental observation of the less stable isomer in polar solvents at low temperatures. This trend is explained in terms of enhanced C=O bonding in the hydrogen-bonded thion (selenium) acids, despite the intrinsically less acidic O-H bond of these isomers. In fact, it is generally the case that, between tautomers RC(=X)YH and RC(=Y)XH, the more stable isomer will be the one with smaller, more electronegative atom multiply bonded to carbon, but the other (less stable) tautomer will be the more acidic (that is, the better hydrogen bond donor). Density-functional theory with a good basis set appears capable of excellent descriptions of both the geometries and relative energies of chalcogen-substituted carboxylic acid isomers. Many more calculations are ongoing toward better understanding and characterization of this new class of molecules and its chemistry.

Acknowledgements This work was supported in part by NSF cooperative agreement ACI-9619020 through computing resources provided by the National Partnership for Advanced Computational Infrastructure at the San Diego Supercomputer Center. H.D.D. and T.L.N. are recipients of Roche Carolina

Research Fellowships. D.A.C. acknowledges support from the Francis Marion University Faculty Development Committee.

Supplementary material Archive entries from Gaussian98 optimization and frequency calculations on molecules **1a**, **1b**, **2a**, **2b**, **3a**, **3b**, **4a**, and **4b** are available.

References

1. Kato, S.; Kawahara, Y.; Kageyama, H.; Yamada, R.; Niyomura, O.; Murai, T.; Kanda, T. *J. Am. Chem. Soc.* **1996**, *118*, 1262.
2. Kageyama, H.; Murai, T.; Kanda, T.; Kato, S. *J. Am. Chem. Soc.* **1994**, *116*, 2195.
3. Jemmis, E. D.; Giju, K. T.; Leszczynski, J. *J. Phys. Chem. A* **1997**, *101*, 7389.
4. (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209. (b) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221.
5. Gaussian 98, Revision A.7: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.
6. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.
7. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
8. (a) Pulay, P. In *Modern Theoretical Chemistry*; Schaefer, H.F., Ed.; Plenum Publishing: New York, 1977; Vol 4, pp 153-185. (b) Pople, J. A.; Raghavachari, K.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem. Symp.* **1979**, *13*, 255. (c) Johnson, B. G.; Frisch, M. J. *J. Chem. Phys.* **1994**, *100*, 7429.
9. Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.
10. Saxe, P.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1982**, *77*, 5647.
11. Randhawa, H. S.; Meese, C. O. *J. Mol. Struct.* **1977**, *36*, 25.
12. Hoffman, R. V. *Organic Chemistry: An Intermediate Text*; Oxford University Press: New York, 1997.
13. Bruice, Paula Y. *Organic Chemistry*; Prentice-Hall: Upper Saddle River, New Jersey, 1995.
14. Crouch, W. W. *J. Am. Chem. Soc.* **1952**, *31*, 105.