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Preparation and Properties of Two Novel Selenoacetic Acids: HCF₂C(O)SeH and CICF₂C(O)SeH

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Supporting Information

ABSTRACT: The novel selenocarboxylic Se-acids, $HCF_2C(O)SeH$ and $ClCF_2C(O)SeH$, were prepared by treating the corresponding carboxylic acids with Woollins' reagent. The boiling points were extrapolated from the vapor pressure curves to be 364 and 359 K for $HCF_2C(O)SeH$ and $ClCF_2C(O)SeH$, respectively. Both compounds are unstable at ambient temperatures and decompose to the corresponding seleno anhydrides and release of H_2Se . Hydrolysis results in formation of the carboxylic acids and hydrogen selenide, while



diselenides presumably are obtained by oxidation. The conformational properties of these acids were studied by vibrational spectroscopy in combination with ab initio and DFT methods. IR vapor-phase spectra, Raman spectra of the neat liquids, and IR spectra of the Ar-matrix-isolated compounds deposited at two different nozzle temperatures were interpreted in terms of quenching conformational equilibria. The most stable structure of both acids was found to be syn-gauche in equilibrium with a second anti-syn form in $HCF_2C(O)SeH$ and with another two conformers, anti-gauche and anti-syn, in $ClCF_2C(O)SeH$.

INTRODUCTION

Recently, we succeeded in the preparation of small selenocarboxylic *Se*-acids, like selenoacetic *Se*-acid in its normal and perdeutereted forms, $CH_3C(O)SeH$ and $CD_3C(O)SeD$,¹ and the trifluoroselenoacetic *Se*-acid, $CF_3C(O)SeH$.² An important role of these molecules in chemical synthesis, particularly in reactions involving $CX_3C(O)Se-$ group transfer, may be anticipated by comparison with reported applications of the sulfur derivatives.³⁻⁵

 $CX_3C(O)SeH^{1,2}$ molecules, like $CX_3C(O)OH^{6,7}$ and $CX_3C(O)SH^{8-10}$ compounds, present a preferred syn conformation (the C=O double bond syn with respect to the Se-H single bond) in equilibrium with the anti form. If one of the X atoms of the CX_3 group is replaced by another Y atom, the conformational possibilities are increased, depending on the orientation of the C-Y bond with respect to the C=O group. Several examples of molecules with general formula $YCX_2C(O)OH$ and $YCX_2C(O)SH$ reported in the literature occur as an equilibrium mixture of two or more rotamers.¹¹⁻¹⁷

Vibrational spectroscopy has been extensively used as a powerful tool to probe their structure, particularly when combined with theoretical studies. IR spectra of compounds isolated in matrices after passing the spray-on nozzle at different temperatures usually contain valuable information about the conformational equilibrium, even for molecules possessing more than two forms in equilibrium. In this paper we report the preparation of two hitherto unknown selenocarboxylic *Se*-acids, $HCF_2C(O)SeH$ and $ClCF_2C-(O)SeH$, by reaction of the corresponding carboxylic acids with Woollins' reagent, $Ph_2P_2Se_4$. The vapor pressure curves and extrapolated boiling points of both compounds were determined. Vibrational properties were studied by IR vapor-phase spectra, Raman spectra of the neat liquids, and IR spectra of the Ar-matrix-isolated compounds deposited at two different nozzle temperatures. Experimental results were interpreted in terms of conformational equilibria aided by ab initio and DFT calculations.

EXPERIMENTAL SECTION

Chemicals. Commercially available difluoroacetic acid and chlorodifluoroacetic acid were purified by repeated trap-to-trap condensation in vacuum. Woollins' reagent, $Ph_2P_2Se_4$, was prepared according the reported procedure.¹⁸

Preparation. Difluoroselenoacetic *Se*-acid, HCF₂C(O)SeH, was prepared by treating HCF₂C(O)OH with an excess of Woollins' reagent^{18–20} at 70 °C in a closed glass vessel. The progress of the reaction was followed by vapor-phase IR spectroscopy. After 10 h the components of the reaction mixture were separated by repeated trapto-trap fractional condensation in vacuum. A pure sample of the compound was retained in the -110 °C trap. Starting from about 11 mmol

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of $HCF_2C(O)OH$, approximately 0.6 mmol of pure $HCF_2C(O)SeH$ was obtained. For spectroscopical studies the products of several preparations were collected together.

Chlorodifluoroselenoacetic acid, ClCF₂C(O)SeH, was prepared in the same way by treating the corresponding carboxylic acid, ClCF₂C-(O)OH, with Woollins' reagent. In this case the reaction was interrupted after 19 h and a pure sample of the compound retained in a trap held at -100 °C. Starting from about 8.0 mmol of ClCF₂C(O)OH, approximately 0.1 mmol of pure ClCF₂C(O)SeH was obtained.

Vapor Pressure. The vapor pressure of the liquid samples was measured in a small vacuum line equipped with a calibrated capacitance manometer (MKS Baratron, AHS-, AHS-100) and a sample reservoir.

NMR Spectroscopy. For the ¹H, ¹⁹F, and ¹³C NMR measurements neat samples were held in flame-sealed, thin-walled 4 mm tubes which were placed inside 5 mm NMR tubes. CD₃OD was used as external lock and TMS and CFCl₃ as reference. Spectra were recorded with a Bruker Avance 250 spectrometer operating at 250.13, 235.36, and 62.90 MHz for ¹H, ¹⁹F, and ¹³C spectra, respectively. Samples were maintained at -30 °C during the measurements.

UV–Vis Spectroscopy. UV–vis spectra of gaseous samples were recorded using a glass cell (optical path length 10 cm) equipped with quartz windows and placed in the sample compartment of a Lambda 900 spectrometer (Perkin-Elmer, Norwalk, CT). Measurements were carried out in the spectral range 200–600 nm.

Vibrational Spectroscopy. IR spectra of the vapor samples were recorded at a resolution of 2 cm⁻¹ in the range 4000-400 cm⁻¹ with a Bruker Vector 25 spectrometer. Raman spectra were measured on neat liquids sealed in 4 mm glass tubes using a Bruker-Equinox 55 FRA 106/S FT-Raman spectrometer and a 1064 nm Nd:YAG laser (150 mW).

Matrix Measurements. A few milligrams of each of the pure compounds were transferred into a small U trap connected to the inlet nozzle of the matrix apparatus. A gas stream of Ar $(2 \text{ mmol } \text{h}^{-1})$ was directed over the sample held at 158 K, and the resulting gas mixture at room temperature was condensed onto a rhodium-plated copper mirror held at 15 K. For experiments at higher temperatures of the gas mixture the nozzle (i.d. 4 mm, length 20 mm quartz tube with an end orifice of 1 mm) was heated to 573 (HCF₂C(O)SeH) or 483 K (ClCF₂C(O)SeH). Details of the matrix apparatus are given elsewhere.²¹ IR spectra of the Ar matrices were recorded in the reflectance mode by means of a transfer optic using the Bruker IFS 66v spectrometer. An MCT-600 detector, together with a KBr/Ge beam splitter, was used in the region 5000–650 cm⁻¹. One hundred scans were added for spectra with apodized resolutions of 0.5 and 0.15 cm⁻¹.

Theoretical Calculations. All quantum chemical calculations were performed with the Gaussian 03 program package.²² Second-order Moller–Plesset (MP2) and density-functional (DFT) B3LYP methods were employed using the $6-311++G^{**}$ basis set. Geometries were optimized by standard gradient techniques with simultaneous relaxation of all geometric parameters.

RESULTS AND DISCUSSION

Difluoroselenoacetic Se-acid, HCF₂C(O)SeH, melts at 148 (2) K, and the vapor pressure curve in the temperature range 214–290 K follows the equation $\ln p$ [atm] = 11.31 – 4117/ *T* [K], giving an extrapolated boiling point of 364 K (see Figures S1 and S2 in the Supporting Information). The vapor pressure curve of chlorodifluoroselenoacetic Se-acid, ClCF₂C-(O)SeH, follows the equation $\ln p$ [atm] = 12.51 – 4494/*T* [K] in the temperature range 236–290 K, giving an extrapolated boiling point of 359 K (see Figures S3 and S4 in the Supporting Information).

Both compounds are unstable at ambient temperatures in sealed glass vessels, giving an orange solid (presumably seleno-anhydride) and H_2Se , detected by its gas-phase IR spectrum.



Figure 1. Gas-phase FTIR spectrum of HCF₂C(O)SeH recorded at 4.7 mbar, 2 cm⁻¹ resolution and an optical path length of 20 cm (top), and Raman spectrum of the liquid recorded at room temperature and using $\lambda = 1064$ nm excitation and 150 mW (bottom).



Figure 2. FTIR spectrum of $HCF_2C(O)SeH$ isolated in solid Ar (bottom) and calculated with the B3LYP/6-311++G** level of approximation (top).

Exposure of the samples to air results in decomposition of the compounds, leading apparently to the corresponding diselenide compounds. $CH_3C(O)SeSeC(O)CH_3$ was identified through its IR and Raman spectra when the selenoacetic *Se*-acid, $CH_3C(O)SeH$, was treated in the same way.²³ Hydrolysis of HCF₂C-(O)SeH and ClCF₂C(O)SeH yields the carboxylic acids and hydrogen selenide, as characterized by their IR spectra in the gas phase.

NMR Spectroscopy. The ¹H NMR spectrum of neat ClCF₂C(O)SeH shows a singlet at 2.8 ppm, which is close to the reported chemical shift for CF₃C(O)SeH (3.1 ppm),² and in the range previously reported for related selenocarboxylic *Se*-acids RC(O)SeH.²⁴ The ¹⁹F NMR spectrum reveals a singlet at -64.8 ppm, which has been assigned to the two fluorine atoms of the ClCF₂- group. This value is 13.8 ppm shifted to higher frequency with respect to the observed signal for CF₃C(O)-SeH, occurring at -78.6 ppm.²

Table 1. Experimental and Calculated Vibrational Wavenumbers (in cm⁻¹) of HCF₂C(O)SeH (relative intensities are given in parentheses)

| | experimental | | MP2/6-31 | | |
|------------|--------------|---|--------------|--------------|--|
| vapor IR | liquid Raman | Ar matrix | syn-gauche | anti-syn | assignment ^b |
| 3468 (2) | | | | | 2 <i>v</i> (C=O) s-g |
| | | 2997.0 (8) | | 3180.2 (5) | ν (C–H) a-s |
| 2988 (3) | 2992 (33) | 2994.0 (10) | 3175.9 (7) | | ν (C–H) s-g |
| 2343 (<1) | | 2316.2 (<1) | | 2540.9 (2) | ν (Se–H) a-s |
| 2333 (<1) | 2323 (100) | 2301.9 (<1) | 2533.3 (3) | | ν (Se–H) s-g |
| 1747 (100) | 1719 (15) | $ \begin{array}{c} 1735.9\\ 1734.0\\ 1730.8 \end{array} $ (100) | 1744.1 (100) | | ν(C==0) s-g |
| | 1679 (6) | 1724.8 (21) | | 1738.7 (100) | ν (C=O) a-s |
| | | 1718.8 (5) | | | ν (C=O) dimer? |
| | | $ \frac{1355.2}{1351.1} $ (1) | | | $\delta(\text{HCF})$ dimer? |
| | 1365 (3) | 1346.6 (6) | 1392.3 (9) | | $\delta(\text{HCF})$ s-g |
| | | 1345.4 1344.5 (4) | | 1385.3 (4) | $\delta(\mathrm{HCF})$ a-s |
| | | 1342.8 (2) | | | $\delta(\text{HCC})$ dimer? |
| 1341 (24) | 1341 (11) | 1335.3 (22) | 1381.9 (14) | | $\delta(\text{HCC})$ s-g |
| | | $\frac{1333.2}{1330.8}$ (4) | | 1372.0 (16) | $\delta(\text{HCC})$ a-s |
| | | 1163.1 (3) | | 1198.5 (31) | $\nu(C-C)$ a-s |
| 1155 (34) | 1152 (9) | 1159.9 (32) | 1197.5 (40) | | ν (C–C) s-g |
| | | $1154.8 \\ 1148.1 $ (19) | | | ν (C–C) dimer? |
| 1096 (52) | | 1103.3 (73) | 1126.7 (57) | | $\nu_{\rm s}(\rm CF_2)$ s-g |
| | | 1097.6 1094.6 (16) | | 1113.9 (11) | $\nu_{\rm s}({\rm CF}_2)$ a-s |
| | | 1087.4 1081.2 (27) | | 1108.0 (75) | $ u_{\rm as}({\rm CF_2})$ a-s |
| 1075 (25) | | $\begin{pmatrix} 1061.0\\ 1059.3 \end{pmatrix}$ (29) | 1093.0 (50) | | $ u_{\rm s}({\rm CF_2}) { m s-g}$ |
| | | 797.4 (1) | | | δ (HSeC) dimer? |
| | | 786.7 (7) | | 855.7 (2) | $\delta(ext{HSeC})$ a-s |
| 795 (6) | 797 (12) | 785.6 (4) | 852.9 (3) | | $\delta(ext{HSeC})$ s-g |
| 712 (6) | | 687.6 (13) | 692.1 (19) | | $\delta 	ext{oop}(ext{CO})$ s-g |
| 678 (4) | | 685.3 (5) | | 662.9 (<1) | $\delta 	ext{oop}(ext{CO})$ a-s |
| 607 (1) | | 610.3 (<1) | | 624.2 (2) | $\delta(ext{OCC})$ a-s |
| 594 (2) | 603 (39) | 602.5 (6) | 610.7 (2) | | $\delta(ext{OCC})$ s-g |
| | | 550.9 (8) | | 562.0 (34) | $\nu_{\rm s}({\rm C-Se})$ a-s |
| 541 (12) | | 546.8 (4) | 520.0 (34) | | $\nu_{\rm s}({\rm C-Se})$ s-g |
| | 440 (15) | | 466.5 (2) | 446.7(2) | $\delta(\mathrm{CF}_2)$ |
| | 349 (37) | | 351.8 (<1) | 288.6 (<1) | $\delta(\mathrm{CF}_2)$ |
| | | | 329.2 (5) | 339.0 (<1) | $\delta({ m SeCO})$ |
| | | | 234.6 (1) | 207.9 (2) | $\delta(\mathrm{CF}_2)_{\mathrm{twist}}$ |
| | | | 162.6 (1) | 166.7 (1) | $\delta({ m SeCC})$ |
| | | | 312(1) | 289(2) | τ |

Relative intensities between parentheses. ${}^{b}s$ -g = syn-gauche, a-s = anti-syn.

The ¹³C NMR spectrum has two triplets centered at 119.4 (${}^{1}J_{(C-F)} = 305.7 \text{ Hz}$) and 185.8 (${}^{2}J_{(C-C-F)} = 37.7 \text{ Hz}$) ppm, which were assigned to the carbon atom of the

 $ClCF_2-$ and C=O groups, respectively. These results are consistent with reported values for related mole-cules.^{25,26}

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Figure 3. Gas-phase FTIR spectrum of ClCF₂C(O)SeH recorded at 9.3 mbar, 2 cm⁻¹ resolution and an optical path length of 20 cm (top), and Raman spectrum of the liquid at room temperature and using $\lambda =$ 1064 nm excitation and 150 mW (bottom).



Figure 4. FTIR spectrum of $ClCF_2C(O)SeH$ isolated in solid Ar (bottom) and calculated with the B3LYP/6-311++G** level of approximation (top).

UV–Vis Spectroscopy. Vapor-phase UV–vis spectra of both selenoacetic *Se*-acids were recorded in the range from 200 to 600 nm. A broad absorption centered at 252 and 253 nm for HCF₂C(O)SeH and ClCF₂C(O)SeH, respectively, was attributed to the $lp(\pi)_{Se} \rightarrow \pi^*_{C=O}$ transition (spectra are presented in Figures S5 and S6, Supporting Information). These values are very close to the 251 nm UV absorption reported for trifluoroselenoacetic *Se*-acid,² indicating similar inductive effects of the CF₃, HCF₂, and ClCF₂ groups on the π lone pair orbital located at the Se atom.

Vibrational Spectroscopy. The vibrational properties of both species were studied through the IR spectra of the vapor phase, Raman spectra of the liquid samples, and IR spectra of Ar-matrix-isolated compounds deposited at two different nozzle temperatures. Spectra were interpreted and assigned based on (i) comparison with related molecules, (ii) theoretically Article



Figure 5. B3LYP/6-311++G** molecular models for the syn-gauche (left) and anti-syn (right) conformers of $HCF_2C(O)SeH$.



Figure 6. B3LYP/6-311++G** molecular models for the syn-gauche (left), anti-gauche (middle), and anti-syn (right) conformers of $ClCF_2C(O)SeH$.

predicted spectra, (iii) relative band intensity changes observed in the matrix spectra at different nozzle temperatures, and (iv) the photochemical behavior of the bands.²⁷

The vapor-phase IR and Raman spectra of liquid HCF_2C -(O)SeH are presented in Figure 1, while Figure 2 shows the Ar-matrix IR spectrum taken at ambient temperature of the sprayon nozzle and the one simulated by DFT calculations. Table 1 compiles the experimental wavenumbers together with the calculated ones obtained by ab initio methods (see the Theoretical Calculations section) and presents a tentative assignment.

Spectra were assigned by comparison with theoretical calculations, which predict the most stable syn-gauche conformer in equilibrium with an anti-syn form (see the Theoretical Calculations section). Fourteen (12) of the 18 vibrational normal modes of the most (less) stable rotamer were observed.

The C–H stretching fundamental is clearly observed at 2992 cm⁻¹ in the Raman spectrum and at 2988 cm⁻¹ in the vapor-IR spectrum as a weak absorption. However, two bands are discernible in the matrix spectra at 2997.0 and 2994.0 cm⁻¹. Taking into account the increase of the relative intensity of the 2997.0 cm⁻¹ absorption at the expense of the 2994.0 cm⁻¹ IR matrix feature when the temperature of the spray-on nozzle was raised from ambient temperature to 583 K and the +4 cm⁻¹ shift predicted by the MP2/6-311++G^{**} method for the second form with respect to the most stable one, these two absorptions were assigned to the anti-syn and syn-gauche conformer, respectively.

The Raman spectrum of the liquid sample is dominated by a strong band centered at 2323 cm⁻¹, attributed to the ν Se–H fundamental mode. A splitting of this band in the IR spectra (vapor-phase, Ar matrix) indicates the presence of two conformers.

The most intense absorption in the vapor-phase IR spectrum corresponds to the ν C=O vibrational mode, occurring at 1747 cm⁻¹ as a unique peak. In the Raman spectrum two bands are detectable in this spectral region. The matrix spectra taken after passing the gas mixture to a nozzle at different temperatures also proved the presence of two conformers, as presented in Table 1.

A sharp peak with medium intensity appears at 1341 cm⁻¹ in the IR spectrum of the vapor and at the same position in the Raman spectrum of the liquid and was assigned to δ (HCC) of the syn-gauche form. The bands corresponding to both

Table 2. Experimental and Calculated Vibrational Wavenumbers (in cm^{-1}) of $ClCF_2C(O)SeH$ (relative intensities are given in parentheses)

| | experimental | | | MP2/6-311++G** ^a | | |
|----------------------------------|----------------------|------------------------------------|-------------------|-----------------------------|--------------|--|
| vapor IR | liquid Raman | Ar matrix | syn-gauche | anti-gauche | anti-syn | $assignment^b$ |
| 3492 (1) | | | | | | 2ν (C=O) s-g |
| 2340 (1) | 2329 (100) | | 2535.6 (2) | 2551.2 (2) | 2542.9 (3) | ν (Se-H) |
| | | 1748.2) | | | 1757.4 (100) | ν (C=O) a-s |
| | | 1745.7 (42) | | | | |
| 1759 (100) | 1731 (13) | 17401(93) | 17571(100) | | | $\nu(C=0)$ s-g |
| 1754(40) | 1/01 (10) | 17377(44) | 1/5/11 (100) | 1752.7(100) | | $\nu(C=0)$ arg |
| 1/01 (10) | | 1216.2(15) | 1240.7 (33) | 1,02., (100) | | $\nu(C-C) a - \sigma$ |
| 12.08 (27) | 1202 (4) | 1216.2(10) 1214.1(30) | 121017 (00) | 1235.5 (31) | | $\nu(C-C) s-g$ |
| 1200 (27) | 1202 (1) | 1211.0(24) | | 120010 (01) | 1197.7 (38) | $\nu(C-C)$ a-s |
| 1160 (64) | 1150 (2) | 1158.8 (98) | 1179.2 (74) | | | ν (CF ₂) s- σ |
| | 1100 (2) | 1156.3 (53) | ((1) | 1174.2 (55) | | $\nu_{as}(CF_2) \circ g$ $\nu_{as}(CF_2) a - g$ |
| | | 1152.6 (26) | | 11, 112 (00) | 1121.4 (90) | $\nu_{as}(CF_2) \approx g$ $\nu_{as}(CF_2) \approx g$ |
| 1055 (12) | 1056 (3) | 1033.8) | | | 1107.6 (46) | $\nu_{as}(CE_2) = 0$ |
| 1055 (12) | 1050 (5) | 1035.6 | | | 110/.0 (10) | $\nu_{s}(OI_{2})$ us |
| | | 1031.0 (17) | | | | |
| | | 1028.7) | | | | |
| 1016 (46) | 1011 (5) | 1014.1 (56) | 1052.5 (96) | | | $\nu_{\rm s}({\rm CF}_2)$ s-g |
| | | 1013.2 | | | | |
| | | 1003.5 | | 1041.4 (83) | | $\nu_{\rm s}({\rm CF_2})$ a-g |
| | | 998.8 { (22) | | | | |
| | | 996.0 | | | | |
| | | 877.1) | | 906.0 (51) | | $\delta(CF_2)_{wag}$ a-g |
| | | 875.1 (10) | | | | |
| | | 873.5 | | | | |
| 873 (29) | 847 (5) | 856.3 (100) | 899.3 (69) | | | $\delta(CE_2)$ s-g |
| 853 (75) | | 843.1 (81) | 0))10 (0)) | | 892.8 (45) | $\delta(CE_2)_{wag} \circ g$ |
| 762(7) | | 7667) | | 804.2 (33) | 0)210 (10) | $\delta(\text{HSeC})$ a-g |
| ,02()) | | 760.7 (4) | | (00) | | 0(11000) # g |
| 742 (24) | $\pi(\epsilon(0))$ | 702.4) | 79(1(40)) | | | S(11C+C) |
| /43 (24) | /05 (8) | 748.4 | /80.1 (49) | | | o(HSeC) s-g |
| | | 747.0 { (19) | | | | |
| | | 740.0 J | | | | |
| 723 (14) | | 728.3 | | | 752.6 (81) | $\delta(ext{HSeC})$ a-s |
| | | 723.8 (6) | | | | |
| | | 720.5 | | | | |
| | | 663.6 (6) | | | 674.3 (2) | $\delta 	ext{oop}(ext{CO})$ a-s |
| 665 (9) | 667 (41) | 661.0 (3) | 673.6 (8) | | | $\delta 	ext{oop}(ext{CO})$ s-g |
| | | 657.2 (1) | | 672.5 (6) | | $\delta 	ext{oop}(ext{CO})$ a-g |
| | | 587.5 (5) | | | 668.8 (<1) | ν (C–Cl) a-s |
| 588 (4) | 592 (12) | 585.7 | 599.9 (4) | | | ν (C–Cl) s-g |
| | | 583.8 | | | | |
| | | 581.5 (3) | | 601.7 (4) | | ν (C–Cl) a-g |
| 488 (4) | 490 (13) | | 508.7 (6) | 494.3 (3) | 463.6 (2) | $\delta(OCSe)$ |
| 425 (1) | 427 (22) | | 438.9 (1) | 437.0 (<1) | 443.4 (2) | ν (C–Se) |
| | 384 (30) | | 389.1 (1) | | | $\delta_{\rm s}({\rm CF}_2)$ |
| | 373 (16) | | 348.1 (<1) | 288.6 (1) | 349.0 (1) | τ (HSeCO) |
| | 343 (19) | | 334.0 (4) | 348.6 (<1) | 290.8 (1) | $\delta(\text{OCC})$ |
| | 280 (15) | | 280.1 (2) | 276.6 (2) | 227.1 (<1) | $\delta_{\rm s}({\rm CF}_2)_{\rm twist}$ |
| | 190 (12) | | 185.3 (<1) | 187.7 (2) | 215.6 (3) | δ (ClCC) |
| | 156 (10) | | 160.7 (<1) | 158.7 (1) | 162.2 (2) | $\delta(\text{SeCC})$ |
| | | | 33.5 (<1) | 40.4 (<1) | 27.6 (1) | τ |
| ^a Relative intensitio | es between parenthes | ses. ^b s-g = syn-gauche | , a-s = anti-syn. | | | |

conformers are observed in the spectrum of the matrix-isolated species, as predicted by ab initio calculations.

Three absorptions, at 1155, 1096, and 1075 cm⁻¹, appear in the 1200–1000 cm⁻¹ region of the IR spectrum. These bands were assigned to ν C–C, ν_{as} CF₂, and ν_{s} CF₂, respectively, by

comparison with the IR spectra of related molecules (see, for example, ref 28) and taking into account the prediction of theoretical calculations. As expected, a more complex pattern was observed in this spectral region in the IR spectra of matrix-isolated HCF₂C(O)SeH. Not only the normal modes of the

Scheme 1. Possible Conformations of Molecules with the General Formula YCX₂C(O)EH



Table 3. Experimental and Calculated Molar Ratios and Theoretically Predicted Relative Energies and Free Energies of the syn-gauche and anti-syn Rotamers of $HCF_2C(O)SeH$

| | 298 | 298 K | | 3 K | | |
|------------------------|-------|-------|-------|-------|-------------------------|----------------------------------|
| | % s-g | % a-s | % s-g | % a-s | ΔE^{a} [kJ/mol] | $\Delta G^{\circ a}$ [kJ/mol] |
| Ar matrix ^b | 84.5 | 15.5 | 83.6 | 16.4 | | |
| MP2/6-311+ +G** | 68.9 | 31.1 | 67.8 | 32.2 | 0.25 | 0.25 |
| B3LYP/6-311+ +G** | 73.0 | 27.0 | 70.1 | 29.9 | 0.29 | 0.75 |

^aRelative energy of the anti-syn (a-s) rotamers with respect to the most stable syn-gauche (s-g) including ZPE corrections. ^bExperimental values are obtained from integrated intensities of the ν (C=O) absorptions in the Ar-matrix IR spectra corrected by calculated absorption coefficients obtained at the B3LYP/6-311++G** level.

most stable conformer but also the ones attributable to the anti-syn form are present in the spectra. According to MP2 prediction, the order of the symmetric and antisymmetric stretching of the CF_2 group is inverted for the second conformer with respect to the most stable one (see Table 1). Only the ν C–C mode, occurring at 1152 cm⁻¹, is observed in the Raman spectrum in this region.

The ν C–Se fundamental was observed only in the IR spectra, appearing at 541 cm⁻¹ in the vapor-phase spectrum and at 546.8 (syn-gauche) and 550.9 (anti-syn) cm⁻¹ in the IR matrix spectra. Bands at lower wavenumbers were assigned to deformation and torsional modes as described in Table 1.

In addition to the absorptions assigned to the syn-gauche and anti-syn forms of $HCF_2C(O)SeH$, some low-intensity features observed in the IR matrix spectra that decrease their intensity with the increase of the nozzle temperature were tentatively assigned to a hydrogen-bonded dimer. The wavenumbers and the proposed assignment were included in Table 1.

The IR vapor-phase spectrum of $ClCF_2C(O)SeH$ is shown in Figure 3, together with the Raman spectrum of the neat liquid. Figure 4 depicts the FTIR spectrum of $ClCF_2C(O)SeH$ isolated in solid Ar and the computed spectrum at the B3LYP/ 6-311++G** level of approximation for the theoretically predicted most stable conformer (see the Theoretical Calculations section). Table 2 compiles the experimental wavenumbers of the three spectra, the predicted vibrational frequencies of the different conformers, and a tentative assignment of the bands. The criteria used for the assignment of the bands were the same as those described for vibrational analysis of $HCF_2C(O)SeH$ (vide infra).

The vapor-phase IR spectrum of $ClCF_2C(O)SeH$ is dominated by two strong absorptions in the carbonylic stretching region at 1759 and 1754 cm⁻¹, which were assigned to the syngauche and anti-*gauche* conformers, respectively, according to the MP2 prediction. As can be seen in Table 2, several bands of the vapor-phase IR were attributed to the second anti-*gauche* form.

The FTIR spectra of the Ar-matrix-isolated compound which pass the spray-on nozzle at ambient temperature and also at 483 K before matrix deposition confirm the presence of three conformers in equilibrium. Eight fundamentals of each of the three conformers of $ClCF_2C(O)SeH$ were observed. A complete description of the IR spectra is presented in Table 2.

Table 4. Experimental and Calculated Molar Ratios and Relative Energies of the syn-gauche (s-g), anti-gauche (a-g) and anti-syn (a-s) Rotamers of $ClCF_2C(O)SeH$

| | 298 K | | 483 K | | ΔE^a [kJ/mol] | | | $\Delta G^{\circ a} [kJ/mol]$ | | | | |
|------------------------|-------|-------|-------|-------|-----------------------|-------|------|-------------------------------|------|------|------|------|
| | % s-g | % a-g | % a-s | % s-g | % a-g | % a-s | s-g | a-g | a-s | s-g | a-g | a-s |
| Ar matrix ^b | 69.1 | 22.0 | 8.9 | 56.3 | 29.0 | 14.7 | | | | | | |
| MP2/6-311++G** | 78.8 | 15.6 | 5.6 | 63.2 | 23.2 | 13.6 | 0.00 | 3.85 | 5.44 | 0.00 | 4.02 | 3.39 |
| B3LYP/6-311++G** | 72.6 | 18.2 | 9.2 | 61.0 | 25.9 | 13.1 | 0.00 | 3.27 | 4.98 | 0.00 | 3.43 | 3.39 |

"Relative energy of the less stable rotamers with respect to the most stable syn-gauche (s-g) including ZPE corrections. ^bExperimental values are obtained from integrated intensities of the ν (C=O) absorptions in the Ar-matrix IR spectra corrected by calculated absorption coefficients obtained at the B3LYP/6-311++G** level.

The most distinct feature in the Raman spectrum of ClCF₂C(O)SeH corresponds to the SeH band at 2329 cm⁻¹. In addition, the Raman spectrum provides the vibrational information of the low-energy region, not studied in the IR spectra. Thus, bands at 384, 373, 343, 280, 190, and 156 cm⁻¹ were assigned to the δ_s (CF₂), τ (HSeCO), δ (OCC), δ_s (CF₂)_{twist}, δ (ClCC), and δ (SeCC), respectively.

Theoretical Calculations. Theoretical conformational studies of compounds of the general formula RC(O)EH, with $R = CX_3$ and E = O, S, or Se, predict the most stable syn conformation (the C=O group syn with respect to the E–H single bond) in equilibrium with the anti form. These results are in agreement with the experimental finding for several derivatives of this family: $CH_3C(O)OH$,⁶ $CH_3C(O)SH$,⁸ $CH_3C(O)SeH$,¹ $CF_3C(O)OH$,⁷ $CF_3C(O)SH$,^{9,10} and $CF_3C(O)SeH$.² If one of the X atoms of the –CX₃ group is substituted for another atom Y, the conformational possibilities are increased, and the orientation of the C=O group with respect to the E–H (syn or anti) and the C–Y single bond (syn, gauche, or anti) should be considered, as depicted in the Scheme 1.

Compounds such as chloroacetic acid, $H_2CClC(O)OH$,^{11–14} and chlorodifluorothioacetic *S*-acid, $ClCF_2C(O)SH$,¹⁵ present an important contribution of the anti form in equilibrium with the most stable syn conformer. For $H_2CClC(O)OH$ the antigauche conformation is the second stable form (of a total of three) as derived from the gas electron diffraction¹¹ and microwave¹² analysis as well as matrix isolation results interpreted in terms of computational calculations.^{13,14} On the other hand, the two most stable structures of $ClCF_2C(O)SH$ according to theoretical calculations correspond to the syn-gauche and antigauche forms.¹⁵

The contribution of the anti form in acids possessing the difluoromethyl group, $-\text{HCF}_2$, is also relevant. For example, for $\text{HCF}_2C(O)OH$ gas electron diffraction¹⁶ and microwave¹⁷ results were interpreted in terms of the presence of two forms in equilibrium, although both studies differ in the relative proportion of each conformer.

In this contribution, the conformational properties of HCF₂C(O)SeH and ClCF₂C(O)SeH acids were theoretically investigated using the B3LYP/6-311+G* model through a relaxed bidimensional scan in which the two dihedral angles OCSeH and HCCO or ClCCO for HCF₂C(O)SeH and $ClCF_2C(O)SeH$, respectively, were simultaneously varied in steps of 10° (Figures S7 and S8, Supporting Information). Only two structures, namely, syn-gauche and anti-syn, have been found to be minima at the potential energy surface of the $HCF_2C(O)SeH$ molecule. These structures were then fully optimized using the B3LYP/6-311++G** and MP2/6-311+ +G** theoretical approximations. Computed relative energies and standard Gibbs free energy differences for the two conformers are listed in Table 3, together with the relative abundance of each rotamer at ambient temperature. Figure 5 shows molecular models of the conformers, and Table S1, Supporting Information, compiles their calculated geometrical parameters. These two conformers have also been proposed for difluoroacetic acid, $HCF_2C(O)OH$, according to gas electron diffraction studies.¹⁶

Analysis of the potential energy surface calculated for $ClCF_2C$ -(O)SeH reveals the presence of three minima, corresponding to the syn-gauche, anti-gauche, and anti-syn forms. Full optimization of these conformers using the B3LYP/6-311++G** and MP2/6-311++G** models confirms them as stable structures

(see Figure 6). Table S2, Supporting Information, lists the calculated geometrical parameters, and Table 4 presents calculated relative energies and standard Gibbs free energy differences, together with the Boltzmann distribution at ambient temperature, for the three forms. These theoretical findings are in complete agreement with the conformational behavior reported for ClCF₂C(O)SH based on vibrational analysis and theoretical calculations.¹⁵

Theoretical vibrational spectra of each of the stable conformers of HCF₂C(O)SeH and ClCF₂C(O)SeH were computed at the B3LYP/6-311++G** and MP2/6-311++G** level to characterize them as true minima and to help in the assignment of the experimental IR and Raman spectra. The calculated wavenumbers for the different conformers of HCF₂C(O)SeH are presented in Table 1, while the corresponding data of ClCF₂C(O)SeH are compiled in Table 2.

CONCLUSIONS

Two hitherto unknown compounds of the selenocarboxylic Seacid family, difluoroselenoacetic Se-acid, $HCF_2C(O)SeH$, and chlorodifluoroselenoacetic Se-acid, $CICF_2C(O)SeH$, were prepared by an O/Se exchange reaction using Woollins' reagent and the corresponding carboxylic acid. The physical properties of these two compounds (boiling points and vapor pressure curves) and chemical reactions at ambient temperatures with oxygen and water were studied. The compounds were investigated by vibrational (vapor-phase IR, liquid Raman, and matrixisolated IR) and UV-vis spectroscopies.

The conformational preferences of these acids were proposed based on interpretation of the vibrational spectra, particularly the IR spectra of the compounds isolated in solid Ar at different nozzle temperatures, and with the aid of predictions using ab initio and DFT methods. The most stable structure of both acids was found to be the syn-gauche form. The presence of a second rotamer, with anti-syn conformation, is predicted for HCF₂C(O)SeH and consistent with the experimental finding. In the case of chlorodifluoroselenoacetic *Se*-acid, the anti-gauche and anti-syn forms were detected in equilibrium with the most stable syn-gauche one.

ASSOCIATED CONTENT

Supporting Information

Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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DEDICATION

Dedicated to Prof. Dr. mult. Alois Haas on the occasion of his 80th birthday

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