Inorganic Chemistry

Article

pubs.acs.org/IC

# Preparation and Properties of Two Novel Selenoacetic Acids: $HCF_2C(O)SeH$ and $ClCF_2C(O)SeH$

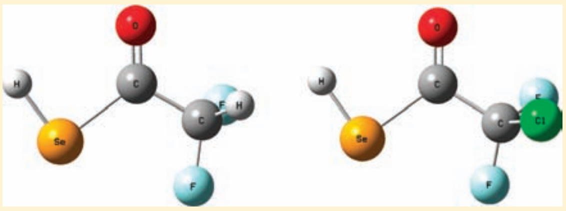
Jovanny A. Gómez Castaño,[†,⊥] Rosana M. Romano,*[,†] Helmut Beckers,[‡] Helge Willner,[‡] and Carlos O. Della Védova[†,§]

[†]CEQUINOR (UNLP-CONICET), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 esq. 115, (1900) La Plata, Argentina

[‡]Anorganische Chemie, Bergische Universität Wuppertal, Gaussstrasse 20, D-42097 Wuppertal, Germany

[§]Laboratorio de Servicios a la Industria y al Sistema Científico (UNLP-CIC-CONICET), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Camino Centenario e/505 y 508, (1897) Gonnet, Argentina

*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 perdeuterated 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, $HCF_2C(O)SeH$, was prepared by treating $HCF_2C(O)OH$ 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 trap-to-trap fractional condensation in vacuum. A pure sample of the compound was retained in the −110 °C trap. Starting from about 11 mmol

**Received:** November 29, 2011
**Published:** February 3, 2012

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, $ClCF_2C(O)SeH$, was prepared in the same way by treating the corresponding carboxylic acid, $ClCF_2C(O)OH$, 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 $ClCF_2C(O)OH$, approximately 0.1 mmol of pure $ClCF_2C(O)SeH$ 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 $^1H$, $^{19}F$, and $^{13}C$ NMR measurements neat samples were held in flame-sealed, thin-walled 4 mm tubes which were placed inside 5 mm NMR tubes. $CD_3OD$ was used as external lock and TMS and $CFCl_3$ as reference. Spectra were recorded with a Bruker Avance 250 spectrometer operating at 250.13, 235.36, and 62.90 MHz for $^1H$, $^{19}F$, and $^{13}C$ 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 mmol $h^{-1}$) 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 ($HCF_2C(O)SeH$) or 483 K ($ClCF_2C(O)SeH$). 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, $HCF_2C(O)SeH$, 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, $ClCF_2C(O)SeH$, 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 selenoanhydride) and $H_2Se$, detected by its gas-phase IR spectrum. 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 $HCF_2C(O)SeH$ and $ClCF_2C(O)SeH$ yields the carboxylic acids and hydrogen selenide, as characterized by their IR spectra in the gas phase.

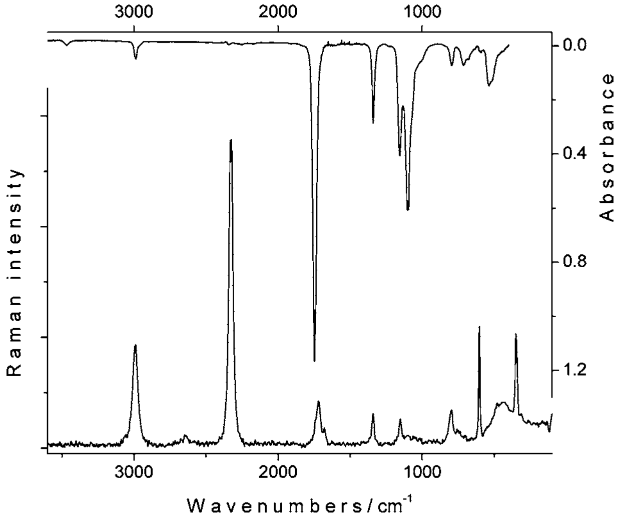


**Figure 1.** Gas-phase FTIR spectrum of $HCF_2C(O)SeH$ recorded at 4.7 mbar, 2 $cm^{-1}$ resolution and an optical path length of 20 cm (top), and Raman spectrum of the liquid recorded at room temperature and using $\lambda$ = 1064 nm excitation and 150 mW (bottom).

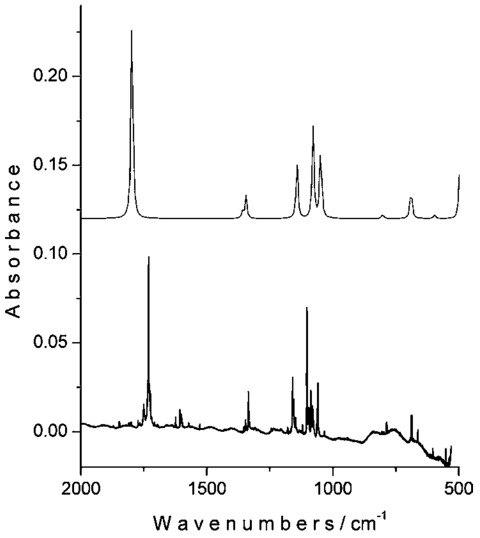


**Figure 2.** FTIR spectrum of $HCF_2C(O)SeH$ isolated in solid Ar (bottom) and calculated with the B3LYP/6-311++G** level of approximation (top).

**NMR Spectroscopy.** The $^1H$ NMR spectrum of neat $ClCF_2C(O)SeH$ shows a singlet at 2.8 ppm, which is close to the reported chemical shift for $CF_3C(O)SeH$ (3.1 ppm),[2] and in the range previously reported for related selenocarboxylic *Se*-acids RC(O)SeH.[24] The $^{19}F$ NMR spectrum reveals a singlet at −64.8 ppm, which has been assigned to the two fluorine atoms of the $ClCF_2$– group. This value is 13.8 ppm shifted to higher frequency with respect to the observed signal for $CF_3C(O)SeH$, occurring at −78.6 ppm.[2]

Table 1. Experimental and Calculated Vibrational Wavenumbers (in $\mathrm{cm^{-1}}$) of $HCF_2C(O)SeH$ (relative intensities are given in parentheses)

| experimental | | | MP2/6-311++G**[a] | | |
|---|---|---|---|---|---|
| vapor IR | liquid Raman | Ar matrix | syn-gauche | anti-syn | assignment[b] |
| 3468 (2) | | | | | 2$\nu$(C=O) s-g |
| | | 2997.0 (8) | | 3180.2 (5) | $\nu$(C−H) a-s |
| 2988 (3) | 2992 (33) | 2994.0 (10) | 3175.9 (7) | | $\nu$(C−H) s-g |
| 2343 (<1) | | 2316.2 (<1) | | 2540.9 (2) | $\nu$(Se−H) a-s |
| 2333 (<1) | 2323 (100) | 2301.9 (<1) | 2533.3 (3) | | $\nu$(Se−H) s-g |
| 1747 (100) | 1719 (15) | 1735.9<br>1734.0 (100)<br>1730.8 | 1744.1 (100) | | $\nu$(C=O) s-g |
| | 1679 (6) | 1724.8 (21) | | 1738.7 (100) | $\nu$(C=O) a-s |
| | | 1718.8 (5) | | | $\nu$(C=O) dimer? |
| | | 1355.2<br>1351.1 (1) | | | $\delta$(HCF) dimer? |
| | 1365 (3) | 1346.6 (6) | 1392.3 (9) | | $\delta$(HCF) s-g |
| | | 1345.4<br>1344.5 (4) | | 1385.3 (4) | $\delta$(HCF) a-s |
| | | 1342.8 (2) | | | $\delta$(HCC) dimer? |
| 1341 (24) | 1341 (11) | 1335.3 (22) | 1381.9 (14) | | $\delta$(HCC) s-g |
| | | 1333.2<br>1330.8 (4) | | 1372.0 (16) | $\delta$(HCC) a-s |
| | | 1163.1 (3) | | 1198.5 (31) | $\nu$(C−C) a-s |
| 1155 (34) | 1152 (9) | 1159.9 (32) | 1197.5 (40) | | $\nu$(C−C) s-g |
| | | 1154.8<br>1148.1 (19) | | | $\nu$(C−C) dimer? |
| 1096 (52) | | 1103.3 (73) | 1126.7 (57) | | $\nu_{as}(CF_2)$ s-g |
| | | 1097.6<br>1094.6 (16) | | 1113.9 (11) | $\nu_{s}(CF_2)$ a-s |
| | | 1087.4<br>1081.2 (27) | | 1108.0 (75) | $\nu_{as}(CF_2)$ a-s |
| 1075 (25) | | 1061.0<br>1059.3 (29) | 1093.0 (50) | | $\nu_{s}(CF_2)$ s-g |
| | | 797.4 (1) | | | $\delta$(HSeC) dimer? |
| | | 786.7 (7) | | 855.7 (2) | $\delta$(HSeC) a-s |
| 795 (6) | 797 (12) | 785.6 (4) | 852.9 (3) | | $\delta$(HSeC) s-g |
| 712 (6) | | 687.6 (13) | 692.1 (19) | | $\delta$oop(CO) s-g |
| 678 (4) | | 685.3 (5) | | 662.9 (<1) | $\delta$oop(CO) a-s |
| 607 (1) | | 610.3 (<1) | | 624.2 (2) | $\delta$(OCC) a-s |
| 594 (2) | 603 (39) | 602.5 (6) | 610.7 (2) | | $\delta$(OCC) s-g |
| | | 550.9 (8) | | 562.0 (34) | $\nu_s$(C−Se) a-s |
| 541 (12) | | 546.8 (4) | 520.0 (34) | | $\nu_s$(C−Se) s-g |
| | 440 (15) | | 466.5 (2) | 446.7(2) | $\delta(CF_2)$ |
| | 349 (37) | | 351.8 (<1) | 288.6 (<1) | $\delta(CF_2)$ |
| | | | 329.2 (5) | 339.0 (<1) | $\delta$(SeCO) |
| | | | 234.6 (1) | 207.9 (2) | $\delta(CF_2)_{twist}$ |
| | | | 162.6 (1) | 166.7 (1) | $\delta$(SeCC) |
| | | | 31.2 (1) | 28.9 (2) | $\tau$ |

[a] Relative intensities between parentheses. [b] s-g = syn-gauche, a-s = anti-syn.

The $^{13}$C NMR spectrum has two triplets centered at 119.4 ($^1J_{(C-F)}$ = 305.7 Hz) and 185.8 ($^2J_{(C-C-F)}$ = 37.7 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 molecules.[25,26]

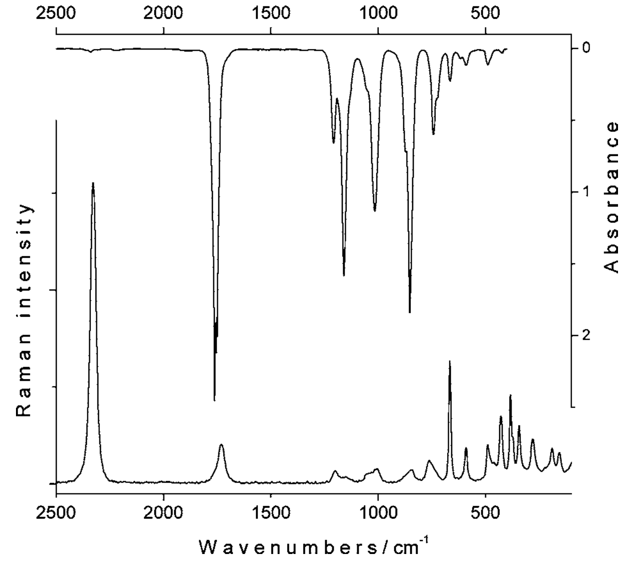


**Figure 3.** Gas-phase FTIR spectrum of $ClCF_2C(O)SeH$ recorded at 9.3 mbar, 2 cm$^{-1}$ resolution and an optical path length of 20 cm (top), and Raman spectrum of the liquid at room temperature and using $\lambda$ = 1064 nm excitation and 150 mW (bottom).

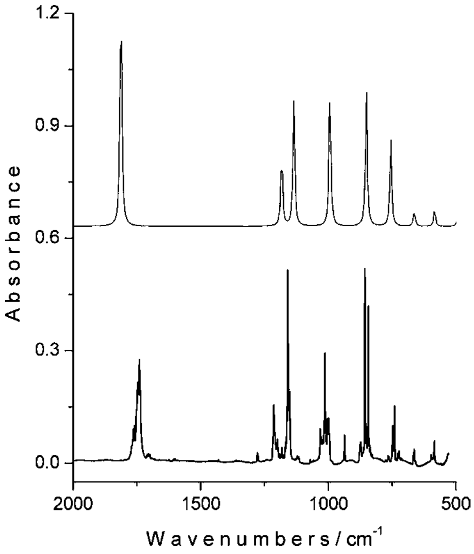


**Figure 4.** FTIR spectrum of $ClCF_2C(O)SeH$ isolated in solid Ar (bottom) and calculated with the B3LYP/6-311++G** level of approximation (top).

**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 $HCF_2C(O)SeH$ and $ClCF_2C(O)SeH$, 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 $CF_3$, $HCF_2$, and $ClCF_2$ groups on the $\pi$ 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 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]

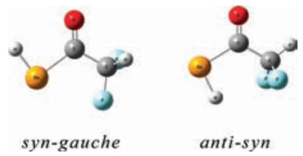


**Figure 5.** B3LYP/6-311++G** molecular models for the syn-gauche (left) and anti-syn (right) conformers of $HCF_2C(O)SeH$.

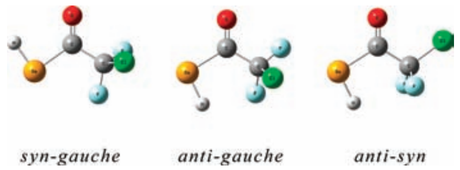


**Figure 6.** B3LYP/6-311++G** molecular models for the syn-gauche (left), anti-gauche (middle), and anti-syn (right) conformers of $ClCF_2C(O)SeH$.

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 spray-on 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 $\nu$ 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 $\nu$ 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 $\delta$(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) | | | | | | $2\nu(C{=}O)$ s-g |
| 2340 (1) | 2329 (100) | | 2535.6 (2) | 2551.2 (2) | 2542.9 (3) | $\nu(Se{-}H)$ |
| | | 1748.2<br>1745.7 } (42) | | | 1757.4 (100) | $\nu(C{=}O)$ a-s |
| 1759 (100) | 1731 (13) | 1740.1 (93) | 1757.1 (100) | | | $\nu(C{=}O)$ s-g |
| 1754 (40) | | 1737.7 (44) | | 1752.7 (100) | | $\nu(C{=}O)$ a-g |
| | | 1216.2 (15) | 1240.7 (33) | | | $\nu(C{-}C)$ a-g |
| 1208 (27) | 1202 (4) | 1214.1 (30) | | 1235.5 (31) | | $\nu(C{-}C)$ s-g |
| | | 1211.0 (24) | | | 1197.7 (38) | $\nu(C{-}C)$ a-s |
| 1160 (64) | 1150 (2) | 1158.8 (98) | 1179.2 (74) | | | $\nu_{as}(CF_2)$ s-g |
| | | 1156.3 (53) | | 1174.2 (55) | | $\nu_{as}(CF_2)$ a-g |
| | | 1152.6 (26) | | | 1121.4 (90) | $\nu_{as}(CF_2)$ a-s |
| 1055 (12) | 1056 (3) | 1033.8<br>1031.6<br>1028.7 } (17) | | | 1107.6 (46) | $\nu_s(CF_2)$ a-s |
| 1016 (46) | 1011 (5) | 1014.1<br>1013.2 } (56) | 1052.5 (96) | | | $\nu_s(CF_2)$ s-g |
| | | 1003.5<br>998.8<br>996.0 } (22) | | 1041.4 (83) | | $\nu_s(CF_2)$ a-g |
| | | 877.1<br>875.1<br>873.5 } (10) | | 906.0 (51) | | $\delta(CF_2)_{wag}$ a-g |
| 873 (29) | 847 (5) | 856.3 (100) | 899.3 (69) | | | $\delta(CF_2)_{wag}$ s-g |
| 853 (75) | | 843.1 (81) | | | 892.8 (45) | $\delta(CF_2)_{wag}$ a-s |
| 762 (7) | | 766.7<br>762.4 } (4) | | 804.2 (33) | | $\delta(HSeC)$ a-g |
| 743 (24) | 765 (8) | 748.4<br>747.0<br>740.0 } (19) | 786.1 (49) | | | $\delta(HSeC)$ s-g |
| 723 (14) | | 728.3<br>723.8<br>720.5 } (6) | | | 752.6 (81) | $\delta(HSeC)$ a-s |
| | | 663.6 (6) | | | 674.3 (2) | $\delta oop(CO)$ a-s |
| 665 (9) | 667 (41) | 661.0 (3) | 673.6 (8) | | | $\delta oop(CO)$ s-g |
| | | 657.2 (1) | | 672.5 (6) | | $\delta oop(CO)$ a-g |
| | | 587.5 (5) | | | 668.8 (<1) | $\nu(C{-}Cl)$ a-s |
| 588 (4) | 592 (12) | 585.7<br>583.8 } (11) | 599.9 (4) | | | $\nu(C{-}Cl)$ s-g |
| | | 581.5 (3) | | 601.7 (4) | | $\nu(C{-}Cl)$ 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) | $\nu(C{-}Se)$ |
| | 384 (30) | | 389.1 (1) | | | $\delta_s(CF_2)$ |
| | 373 (16) | | 348.1 (<1) | 288.6 (1) | 349.0 (1) | $\tau(HSeCO)$ |
| | 343 (19) | | 334.0 (4) | 348.6 (<1) | 290.8 (1) | $\delta(OCC)$ |
| | 280 (15) | | 280.1 (2) | 276.6 (2) | 227.1 (<1) | $\delta_s(CF_2)_{twist}$ |
| | 190 (12) | | 185.3 (<1) | 187.7 (2) | 215.6 (3) | $\delta(ClCC)$ |
| | 156 (10) | | 160.7 (<1) | 158.7 (1) | 162.2 (2) | $\delta(SeCC)$ |
| | | | 33.5 (<1) | 40.4 (<1) | 27.6 (1) | $\tau$ |

[a] Relative intensities between parentheses. [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 $\nu C{-}C$, $\nu_{as}CF_2$, and $\nu_sCF_2$, 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 $HCF_2C(O)SeH$. Not only the normal modes of the

**Scheme 1. Possible Conformations of Molecules with the General Formula $YCX_2C(O)EH$**

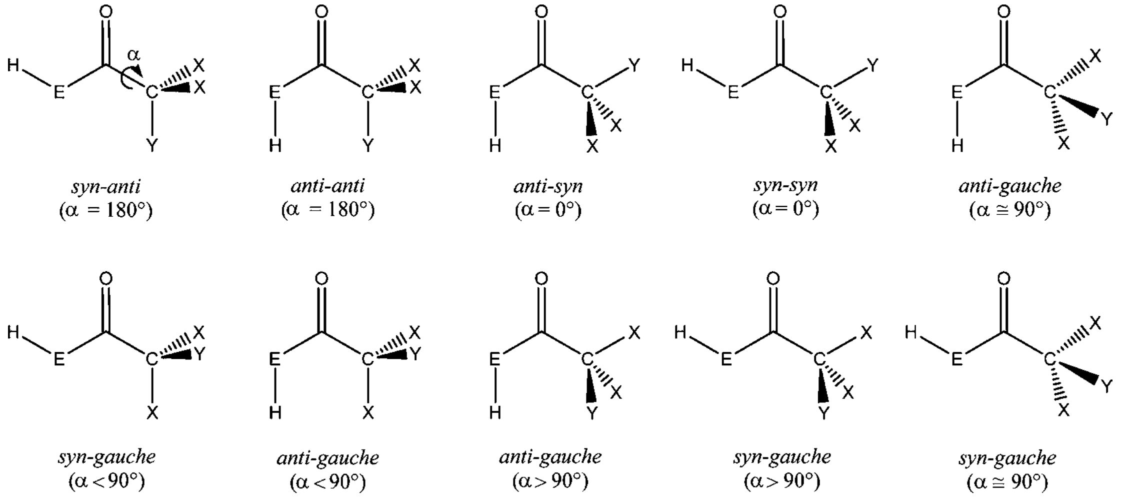


**Table 3. Experimental and Calculated Molar Ratios and Theoretically Predicted Relative Energies and Free Energies of the syn-gauche and anti-syn Rotamers of $HCF_2C(O)SeH$**

| | 298 K | | 573 K | | | |
|---|---|---|---|---|---|---|
| | % s-g | % a-s | % s-g | % a-s | $\Delta E^a$ [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 |

[a] Relative energy of the anti-syn (a-s) rotamers with respect to the most stable syn-gauche (s-g) including ZPE corrections. [b] Experimental values are obtained from integrated intensities of the $\nu$(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 $\nu$C−C mode, occurring at 1152 $cm^{-1}$, is observed in the Raman spectrum in this region.

The $\nu$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 syn-gauche 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 | | | $\Delta E^a$ [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 |

[a] Relative energy of the less stable rotamers with respect to the most stable syn-gauche (s-g) including ZPE corrections. [b] Experimental values are obtained from integrated intensities of the $\nu$(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 $ClCF_2C(O)SeH$ 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 $\delta_s(CF_2)$, $\tau(HSeCO)$, $\delta(OCC)$, $\delta_s(CF_2)_{twist}$, $\delta(ClCC)$, and $\delta(SeCC)$, 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 $-CX_3$ 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 anti-gauche conformation is the second stable form (of a total of three) as derived from the gas electron diffraction[11] and microwave[12] 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 anti-gauche forms.[15]

The contribution of the anti form in acids possessing the difluoromethyl group, $-HCF_2$, is also relevant. For example, for $HCF_2C(O)OH$ gas electron diffraction[16] and microwave[17] 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 $HCF_2C(O)SeH$ and $ClCF_2C(O)SeH$ 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 $HCF_2C(O)SeH$ 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 $ClCF_2C(O)SH$ based on vibrational analysis and theoretical calculations.[15]

Theoretical vibrational spectra of each of the stable conformers of $HCF_2C(O)SeH$ and $ClCF_2C(O)SeH$ 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 $HCF_2C(O)SeH$ are presented in Table 1, while the corresponding data of $ClCF_2C(O)SeH$ are compiled in Table 2.

## ■ CONCLUSIONS

Two hitherto unknown compounds of the selenocarboxylic *Se*-acid family, difluoroselenoacetic *Se*-acid, $HCF_2C(O)SeH$, and chlorodifluoroselenoacetic *Se*-acid, $ClCF_2C(O)SeH$, 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 matrix-isolated 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 $HCF_2C(O)SeH$ 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.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail: romano@quimica.unlp.edu.ar.

### Present Address

⊥Escuela de Ciencias Químicas, Facultad de Ciencias, Universidad Pedagógica y Tecnológica de Colombia (UPTC), Avenida Central del Norte, (150003) Tunja, Boyacá, Colombia.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

C.O.D.V. and R.M.R. thank the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) (PIP 0352), the Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT, PICT 33878 and 322), the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC), and the Facultad de Ciencias Exactas, UNLP for financial support. J.A.G.C. acknowledges an award from the Deutsche Akademische Austauschdienst (DAAD). C.O.D.V. especially acknowledges the DAAD, which generously supported the DAAD Regional Program of Chemistry of the Republic Argentina that encourages Latin-American students to realize their Ph.D. work in La Plata.

## ■ DEDICATION

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

## ■ REFERENCES

(1) Gómez Castaño, J. A.; Romano, R. M.; Beckers, H.; Willner, H.; Boese, R.; Della Védova, C. O. *Angew. Chem., Int. Ed.* **2008**, *47*, 10114−10118.

(2) Gómez Castaño, J. A.; Romano, R M.; Beckers, H.; Willner, H.; Della Védova, C. O. *Inorg. Chem.* **2010**, *49*, 9972−9977.

(3) Rochat, W. V.; Gard, G. L. *J. Org. Chem.* **1969**, *34*, 4173−4176.

(4) Minkwitz, R.; Sawatzki, J. *Z. Anorg. Allg. Chem.* **1988**, *566*, 151−159.

(5) Cunneen, J. I. *J. Chem. Soc.* **1947**, 134−141.

(6) Macoas, E. M. S.; Khriachtchev, L.; Petterson, M.; Fausto, R.; Räsänen, M. *J. Chem. Phys.* **2004**, *121*, 1331−1338.

(7) Stolvijk, V. M.; Van-Eijck, B. P. *J. Mol. Spectrosc.* **1985**, *113*, 196−207.

(8) Romano, R. M.; Della Védova, C. O.; Downs, A. J. *J. Phys. Chem. A.* **2002**, *106*, 7235−7244.

(9) Gobbato, K. I.; Della Védova, C. O.; Mack, H.; Oberhammer, H. *Inorg. Chem.* **1996**, *35*, 6152−6157.

(10) Mollendal, H. *J. Phys. Chem. A* **2007**, *111*, 1891−1898.

(11) Van Eijck, B. P.; Maagdenber, A. A. J.; Wanrooy, J. *J. Mol. Struct.* **1974**, *22*, 61−67.

(12) Derissen, J. L.; Bijen, J. M. *J. Mol Struct.* **1975**, *29*, 153−161.

(13) Nieminen, J.; Pettersson, M.; Räsänen, M. *J. Phys. Chem.* **1993**, *97*, 10925−10936.

(14) Fausto, R.; Macoas, E. M. S.; Kulbida, A. *J. Mol. Struct.* **1999**, *480−481*, 83−99.

(15) Erben, M. F.; Boese, R.; Willner, H.; Della Védova, C. O. *Eur. J. Org. Chem.* **2007**, 4917−4926.

(16) Bijen, J. M.; Derissen, J. L. *J. Mol. Struct.* **1975**, *27*, 233−240.

(17) Van Eijck, B. P.; Maagdenberg, A. A. J.; Janssen, G.; Van Goethem-Wiersma, T. J. *J. Mol. Spectrosc.* **1983**, *98*, 282−303.

(18) Gray, I. P.; Bhattacharyya, P.; Slawin, A. M. Z.; Woollins, J. D. *Chem.—Eur. J.* **2005**, *11*, 6221−6227.

(19) Fitzmaurice, J. C.; Willians, D. J.; Wood, P. T.; Woollins, J. D. *J. Chem. Soc., Chem. Commun.* **1988**, 741−743.

(20) Bhattacharyya, P.; Woollins, J. D. *Tetrahedron Lett.* **2001**, *42*, 5949−5951.

(21) Schnöckel, H.; Willner, H. In *Infrared and Raman Spectroscopy, Methods and Applications*; Schrader, B., Ed.; VCH: Weinheim, 1994; p 297.

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*; Revision B.04 ed.; Gaussian, Inc.: Pittsburgh, PA, 2003.

(23) Gómez Castaño, J. A. Ph.D. Dissertation, University of La Plata, 2009.

(24) Kageyama, H.; Murai, T.; Kanda, T.; Kato, S. *J. Am. Chem. Soc.* **1994**, *116*, 2195−2196.

(25) Jacobsen, N. E. *NMR Spectroscopy Explained. Simplified Theory, Applications and Examples for Organic Chemistry and Structural Biology*; Wiley: New York, 2007; p 61.

(26) Silverstein, R. M; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 5th ed.; Wiley: New York, 1991; pp 246−247.

(27) Gómez Castaño, J. A.; Romano, R. M.; Beckers, H.; Willner, H.; Della Védova, C. O. Unpublished results.

(28) Woodward, A. J.; Jonatnan, N. *J. Mol. Spectrosc.* **1970**, *35*, 127−136.