DOI: 10.1002/anie.200803513

Chalcogenocarboxylic Acids

Selenoacetic Acid, $CH_3C(O)SeH$: Preparation, Characterization, and Conformational Properties**

*Jovanny A. Gómez Castaño, Rosana M. Romano, Helmut Beckers, Helge Willner, Roland Boese, and Carlos O. Della Védova**

Selenocarboxylic acids (RC(O)SeH) and their derivatives have experienced growing interest during the last two decades.[1–8] Some synthetic contributions to aliphatic ($R = C_nH_m$ with $n \geq 2$) and aromatic selenocarboxylic acids have been made by Kato et al.[1–4] In contrast, carboxylic acids (RC(O)OH) and thiocarboxylic acids (RC(O)SH) are common compounds with a wide range of applications. Thioacetic acid, $CH_3C(O)SH$, was first reported in 1854 by Kekule;[9] however, the seleno analogue, $CH_3C(O)SeH$, has been neither isolated nor characterized hitherto. Herein, we describe the preparation of selenoacetic acid in its normal form and in its perdeuterated form, $CD_3C(O)SeD$. We also report its low-temperature single-crystal structure, its physical properties, its vibrational, UV/Vis, and NMR spectra, and its photochemical behavior in matrix isolation.

$CH_3C(O)SeH$ and $CD_3C(O)SeD$ are formed within one day by treatment of $CH_3C(O)OH$ or $CD_3C(O)OD$, respectively, with an excess of Woollins' reagent, $Ph_2P_2Se_4$,[10] at 75 °C in a small pyrex vessel under moisture- and air-free conditions. The progress of the reaction was followed by recording gas-phase FTIR spectra of small samples of the reaction mixture. After 3 hours, a new set of bands (at 1758, 1362, 1110, 1006, 953, and 575 cm^{-1} in the reaction with $CH_3C(O)OH$; and at 1751, 1131, 975, and 522 cm^{-1} in the reaction with $CD_3C(O)OD$) became visible in the IR spectrum of the reaction mixture. The reaction mixture was separated by repeated trap-to-trap fractional condensation in vacuum, and the pure product was retained at −90 °C. In similar earlier studies, Knapp and Darout proposed the intermediate formation of selenocarboxylic acids by treating Woollins' reagent with RC(O)OH, but they did not isolate the compounds.[11]

$CH_3C(O)SeH$ and $CD_3C(O)SeD$ are shiny green liquids at room temperature with a fetid odor characteristic of toxic organoselenium compounds.[12] For $CH_3C(O)SeH$, the melting point is 223 K, and the vapor pressure over the temperature range 248–291 K follows the equation $\ln p = 10.78 - 4111/T$ (p [atm]; T [K]), giving an extrapolated normal boiling point of 382 K (see Figures S1 and S2 in the Supporting Information). The melting and boiling points of $CH_3C(O)SeH$ are lower than those of $CH_3C(O)OH$ (290 and 391 K) because of the much weaker hydrogen bonding in selenoacetic acid. In the presence of air, selenoacetic acid is immediately oxidized to the corresponding yellow diselenide $CH_3C(O)Se_2C(O)CH_3$. Hydrolysis of selenoacetic acid results in the instantaneous formation of acetic acid and hydrogen selenide. Selenoacetic acid is thermally stable at room temperature in a sealed glass vessel for several hours.

Theoretical calculations on selenoacetic acid predict the *syn* form to be more stable than the *anti* form (Figure 1), with an energy difference of 0.67 or 0.94 kcal mol^{-1} at the B3LYP/6-311++G**and MP2/6-311++G** levels of theory, respectively (Table S1 and Figure S3 in the Supporting Information). Gas-phase acidity calculations predict that selenoacetic acid is the strongest acid of the series $CH_3C(O)EH$ ($E = O$, S, Se), followed by thioacetic acid, and acetic acid (Table S2).

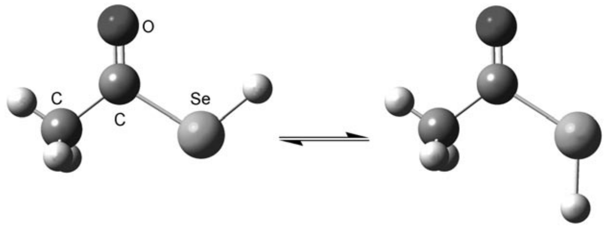


Figure 1. Rotational equilibrium between the *syn* and *anti* forms of $CH_3C(O)SeH$.

---

[*] Lic. J. A. Gómez Castaño, Prof. Dr. R. M. Romano,
Prof. Dr. Dr. C. 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)
E-mail: carlosdv@quimica.unlp.edu.ar
Prof. Dr. Dr. C. O. Della Védova
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
47 esq. 115, 1900 La Plata (Argentina)
Prof. Dr. R. Boese
Institut für Anorganische Chemie, Universität Duisburg-Essen
Universitätsstrasse 5–7, 45117 Essen (Germany)
Dr. H. Beckers, Prof. Dr. H. Willner
Anorganische Chemie, Bergische Universität Wuppertal
Gaußstrasse 20, 42097 Wuppertal (Germany)

[**] C.O.D.V. and R.M.R. thank the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) (PIP 4695), the Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT), the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC), and the Facultad de Ciencias Exactas, UNLP for financial support. R.M.R. is also grateful to the Fundación Antorchas. In addition, J.A.G. acknowledges with thanks a Deutscher Akademischer Austauschdienst (DAAD) award. C.O.D.V. especially acknowledges the DAAD for generously sponsoring the DAAD Regional Program of Chemistry of the Republic of Argentina, which supports Latin-American students earning their PhD in La Plata. R.B. acknowledges support of the DFG-Forschergruppe 618.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200803513.

In the crystal, two independent molecules of selenoacetic acid adopt C_s symmetry according to the space group *Pbcm*. Considering the inherent uncertainty of acidic hydrogen positions close to heavy atoms, *syn–syn* and *anti–anti* conformations are both possible in the present case; *syn–anti* is not feasible. For the calculated acidic proton positions of both of the independent molecules (Se–H 1.46 Å), two packing motifs result. In the *syn–syn* conformation, the structure consists of parallel catemeric chains which employ Se–H···O and Se–H···Se hydrogen bonds (H···O 2.26 Å and H···Se 2.88 Å; Figure 2a); the *anti–anti* conformation displays antiparallel chains with bifurcated Se–H···O(Se) hydrogen bridges (H···O 2.20 Å and H···Se 2.69 Å; Figure 2b). Based on the better *R* value achieved during the refinement (4.75 vs. 4.81 %), a slight preference is given to the *anti–anti* option.

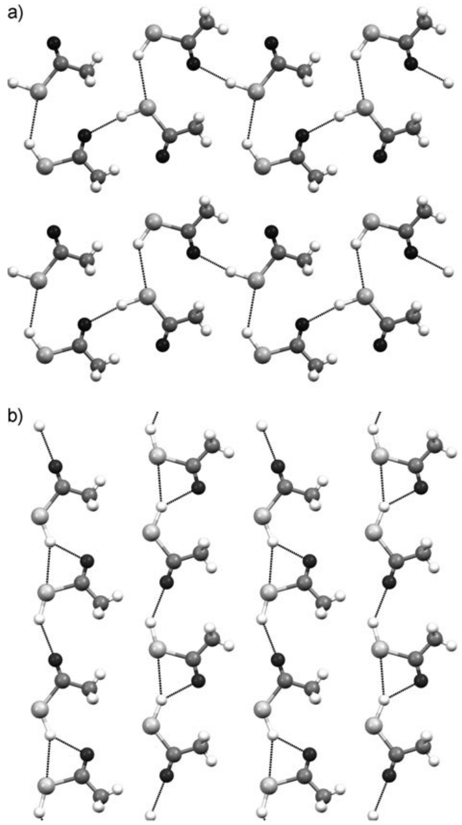


Figure 2. Molecular packing of the two independent molecules as *syn–syn* (a) and the preferred *anti–anti* conformers (b) in crystalline $CH_3C(O)SeH$ at 143(2) K.

As in the case of the $CH_3C(O)OH$[13] and $CH_3C(O)SH$[14] molecules, the $CH_3C(O)SeH$ molecule is expected to have C_s symmetry. According to this assumption, the $CH_3C(O)SeH$ molecule should be characterized by 18 normal modes of vibration, all of which are active to both IR absorption and Raman scattering, and which can be divided into 12 symmetric (a') and 6 antisymmetric (a'') vibrations. The IR spectra of the vapors of $CH_3C(O)SeH$ and $CD_3C(O)SeD$ and Raman spectra of the liquids are presented in Figure 3, and the observed wavenumbers of the vibrational modes of $CH_3C(O)SeH$ are listed, together with calculated values and tentative assignments, in Table 1 (for vibrational spectroscopic data for $CD_3C(O)SeD$, see Table S5 in the Supporting Information). The strongest absorption bands in the IR spectra of the vapors at 1758 and 1753 cm^{-1}, which are matched by weak Raman scattering bands at 1725 and 1724 cm^{-1}, are due to the C=O stretching modes of $CH_3C(O)SeH$ and $CD_3C(O)SeD$, respectively. The most intense band in the Raman spectrum of liquid $CH_3C(O)SeH$ at 2315 cm^{-1}, which has a corresponding weak absorption at 2336 cm^{-1} in the IR spectrum of the vapor, is assigned to the Se–H stretching mode. Similar wavenumbers have been reported for CH_3SeH (2330 cm^{-1} in the IR spectrum of the vapor; 2301 cm^{-1} in the Raman spectrum of the liquid)[15] and H_2Se (2350 cm^{-1} in the IR spectrum of the vapor; 2312 cm^{-1} in the Raman spectrum of the liquid).[16] The Se–D stretching vibration of $CD_3C(O)SeD$ appears at 1668 cm^{-1} in the Raman spectrum of the liquid and at 1694 cm^{-1} in the IR spectrum of the vapor. Similar wavenumbers have been reported for CD_3SeD (1680 cm^{-1} in the IR spectrum of the vapor; 1658 cm^{-1} in the Raman spectrum of the liquid)[15] and D_2Se

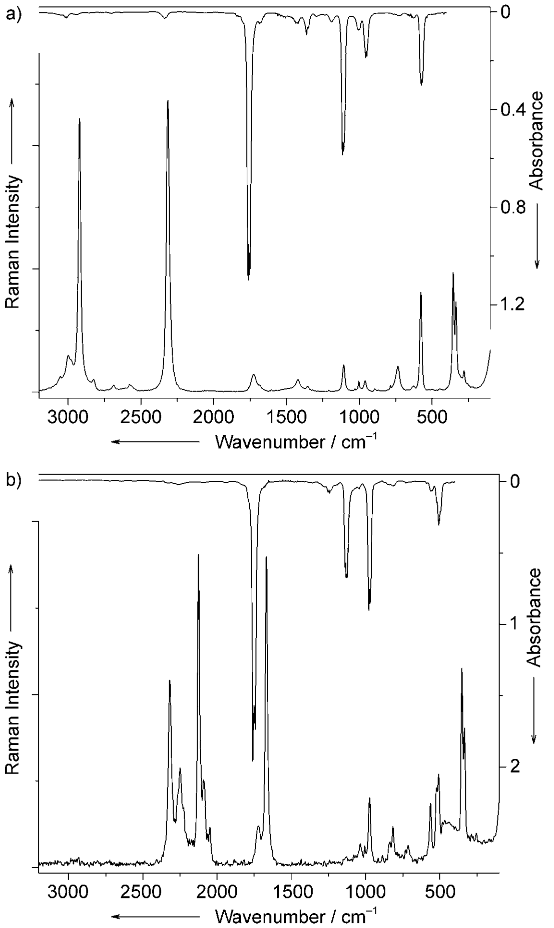


Figure 3. FTIR spectra of the vapors of $CH_3C(O)SeH$ (a; top and right axes) and $CD_3C(O)SeD$ (b; top and right axes) at 3 or 5 mbar, respectively, at a resolution of 2 cm^{-1}, and at an optical path length of 20 cm^{-1}; and Raman spectra of the liquids of $CH_3C(O)SeH$ (a; bottom and left axes) and $CD_3C(O)SeD$ (b; bottom and left axes) at room temperature upon excitation at 1064 nm and 150 mW.

Table 1: Experimental and calculated (B3LYP/6-311++G**) wavenumbers [cm^{-1}] of the vibrational modes of $CH_3C(O)SeH$; relative intensities are given in parentheses.

Experimental			Calculated		Assignment[a]
Vapor IR	Liquid Raman	Ar matrix IR	*syn*	*anti*	
3013	3001	3016.1 (2)	3160.8 (2)		$\nu_a(CH_3)_{syn}$
		3014.1 (1)		3158.8 (2)	$\nu_a(CH_3)_{anti}$
2945	2920	2984.8 (<1)		3125.4 (<1)	$\nu_a(CH_3)_{anti}$
		2965.3 (<1)	3122.2 (1)		$\nu_a(CH_3)_{syn}$
2854	2825	2930.0 (<1)	3055.8 (<1)	3058.2 (<1)	$\nu_s(CH_3)$
2336	2315	2301.4 (<1)	2410.4 (2)		$\nu(Se{-}H)_{syn}$
2325		2293.6 (<1)		2389.2 (7)	$\nu(Se{-}H)_{anti}$
1758	1725	1746.6 (100)	1788.2 (100)		$\nu(C{=}O)_{syn}$
		1740.9 (32)		1780.6 (100)	$\nu(C{=}O)_{anti}$
1444		1446.2 (<1)	1496.5 (4)		$\delta_a(CH_3)_{twist\ syn}$
1436		1439.4 (<1)		1495.9 (4)	$\delta_a(CH_3)_{twist\ anti}$
1422	1422	1423.4 (2)		1486.5 (3)	$\delta_s(CH_3)_{anti}$
		1421.9 (5)	1485.5 (5)		$\delta_s(CH_3)_{syn}$
1362	1354	1351.2 (9)	1409.6 (7)		$\delta_s(CH_3)_{wag\ syn}$
1350		1349.7 (3)		1407.8 (6)	$\delta_s(CH_3)_{wag\ anti}$
1110	1108	1105.8 (91)	1138.4 (2)	1141.2 (37)	$\delta(H{-}C{-}C)$
1006	1004	985.6 (<1)	1042.6 (<1)		$\rho(CH_3)_{syn}$
		982.6 (<1)		1042.5 (<1)	$\rho(CH_3)_{anti}$
953	960	950.2 (7)		978.0 (11)	$\nu(C{-}C)_{anti}$
		945.9 (14)	978.7(19)		$\nu(C{-}C)_{syn}$
730	735	743.4 (<1)		767.5 (3)	$\delta(HSeC)_{anti}$
		727.1 (2)	758.8 (2)		$\delta(HSeC)_{syn}$
575	578	575.6 (10)	586.2 (21)		$\nu(C{-}Se)_{syn}$
		569.1 (3)		595.1 (17)	$\nu(C{-}Se)_{anti}$
481				529.3 (<1)	$\delta_{oop}(C{=}O)_{anti}$
			518.3 (<1)		$\delta_{oop}(C{=}O)_{syn}$
	355		355.0 (<1)	335.8 (1)	$\delta(OCSe)$
	336		336.9 (3)	304.2 (1)	$\tau(HSeCO)$
	280		283.1 (2)	291.0 (<1)	$\delta(SeCC)$
			30.3 (<1)	98.3 (<1)	$\tau(CH_3)$

[a] a = antisymmetric, s = symmetric, oop = out of plane.

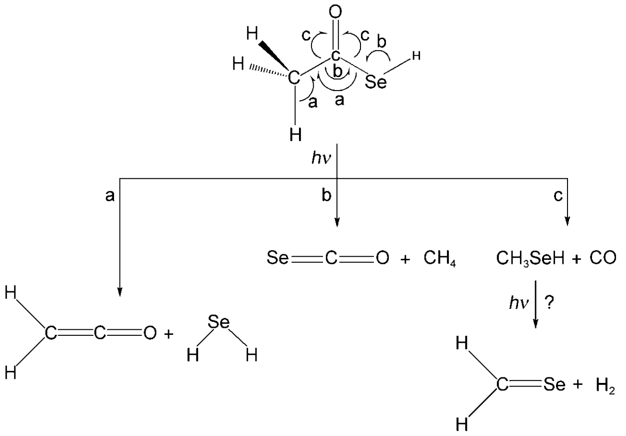
(1696 cm^{-1} in the IR spectrum of the vapor; 1665 cm^{-1} in the Raman spectrum of the liquid).[16]

Additional information on the vibrational modes of $CH_3C(O)SeH$ and $CD_3C(O)SeD$ was obtained from IR spectra of the compounds isolated in an argon matrix at 15 K, in which splitting of nearly all the absorption bands is observed. For instance, the C=O stretching region in the IR spectrum of $CH_3C(O)SeH$, which can be considered as a conformational sensor, shows two bands at 1746.6 and 1740.9 cm^{-1} with an intensity ratio of approximately 3 to 1. The intensity ratio of these absorption bands decreased with increasing temperature of the inlet nozzle (Figure S5 in the Supporting Information), owing to the equilibrium between *syn* and *anti* forms in the gas phase (Figure 1). Assignments of the vibrational modes to the *syn* and *anti* conformers of $CH_3C(O)SeH$ trapped in an argon matrix are also included in Table 1.

In the UV/Vis spectrum of $CH_3C(O)SeH$, a strong absorption band at 200 nm, a weaker band at 234 nm, and a much weaker band at 490 nm are observed. By comparison with the assignments given for the UV/Vis spectra of $CH_3C(O)OH$[17] and $CH_3C(O)SH$,[18] a tentative interpretation involving the electronic transitions $\pi_{C=O} \rightarrow \pi^*_{C=O}$ (200 nm) and $lp\,\pi_{Se} \rightarrow \pi^*_{C=O}$ (234 nm) can be inferred (Figures S6–S8 in the Supporting Information). The uncoupled ^{77}Se NMR spectrum of $CH_3C(O)SeH$ shows a singlet resonance at 434.7 ppm. In the ^{1}H NMR spectrum of $CH_3C(O)SeH$, signals corresponding to three protons and one proton are observed at 2.3 and 4.1 ppm, respectively. In the ^{13}C NMR spectrum of $CH_3C(O)SeH$, two signals of similar intensity are located at 37.8 and 195.6 ppm; distortionless enhancement by polarization transfer (DEPT) experiments indicate that these signals correspond to CH_3 and C=O groups, respectively. Similar values of chemical shift have been reported for $CH_3OC_6H_4C(O)SeH$ in $CDCl_3$ at room temperature (^{77}Se NMR: 427.5 ppm; ^{1}H NMR: 2.59 ppm (SeH); ^{13}C NMR: 189.6 ppm (C=O)).[19]

Exposure of an argon matrix containing $CH_3C(O)SeH$ or $CD_3C(O)SeD$ at 15 K to UV/Vis light results in a rapid decrease (of about 45% after 1 min) of the IR absorption bands belonging to the parent compound, and the appearance of new bands (Figures S9 and S10, and Tables S6 and S7 in the Supporting Information). The strongest new absorption band at 2147.0 cm^{-1} in the IR spectrum of the matrix that contained the precursor $CH_3C(O)SeH$ could have been mistaken as arising from CO (2138.0 cm^{-1}).[20] However, its shift to 2110 cm^{-1} in the IR spectrum of the matrix that contained the precursor $CD_3C(O)SeD$ and the correlated behavior of several other absorption bands leave little doubt that this band arises from a ketene.[21] By grouping the new bands according to their photochemical behavior, taking the effects of perdeuteration of the precursor into account, and by comparing the bands with reported data, the photoproducts H_2Se,[22] CH_3SeH,[15] OCSe,[23] CO,[20] and CH_4[24] can also be identified. The formation of these compounds can be explained on the basis of three different photochemical decomposition channels (Scheme 1) analogous to those observed for the irradiation of $CH_3C(O)SH$ in an argon matrix.[21] In fact, the absorption bands of the ketene and of selenomethanol were observed to decay with longer irradiation times and, starting from $CH_3C(O)SeH$, new weak, broad bands appeared near 2984 and 924 cm^{-1}. A tentative explanation of these bands associates them with the ν_1 (2972.5 cm^{-1}) and ν_4 (916.4 cm^{-1}) modes reported very recently for $H_2C{=}Se$ trapped in an argon matrix.[25]

In summary, the parent selenoacetic acid and its perdeuterated form have been prepared for the first time, and their vibrational, UV/Vis, and NMR spectra, and physical proper-



Scheme 1. Photochemical decomposition of $CH_3C(O)SeH$ isolated in a solid argon matrix at 15 K by three different channels.

ties have been measured. The structure of a single crystal of $CH_3C(O)SeH$ has been determined at low temperature, and FTIR spectroscopy has been used not only to characterize the matrix-isolated molecules $CH_3C(O)SeH$ and $CD_3C(O)SeD$, but also to explore their photochemistry. For each isotopomer, we have been able to identify two conformers (*syn* and *anti*). They coexist in equilibrium in the gas phase and also occur together in the solid phase as hydrogen-bonded dimers forming layer networks. The results of theoretical calculations (B3LYP/6-311++G** and MP2/6-311++G**) conform well to the experimental findings.

Experimental Section

Glacial acetic acid (Cark Roth) was treated with acetic anhydride (5%) and $KMnO_4$ to remove water and oxidizable impurities, respectively. Fractional distillation under an inert atmosphere was performed, and further purification was achieved by repeated trap-to-trap condensation in vacuum. Samples of $CD_3C(O)OD$ for NMR spectroscopy (Merck) were used as received. Both commercial (Aldrich) and synthesized samples of Woollins' reagent, $Ph_2P_2Se_4$,[10c] were used in this study.

The vapor pressure of $CH_3C(O)SeH$ and $CD_3C(O)SeD$ was measured in a small vacuum line equipped with a calibrated capacitance manometer (MKS Baratron, AHS-100) and a sample reservoir. The melting points were determined for small samples of the compounds, each contained in a 4 mm glass tube immersed in a cold bath in a transparent Dewar vessel.

IR spectra of the vapors of $CH_3C(O)SeH$ and $CD_3C(O)SeD$ were recorded at a resolution of $2\ cm^{-1}$ in the wavenumber range 4000–400 cm^{-1} with a Bruker Vector 25 spectrometer. Raman spectra of the liquids sealed in 4 mm glass capillaries were measured with a Bruker-Equinox 55 FRA 106/S FT-Raman spectrometer using a 1064 nm Nd:YAG laser (150 mW).

Matrix measurements: A few milligrams of $CH_3C(O)SeH$ or $CD_3C(O)SeD$ were transferred to a small U-trap connected to the inlet nozzle of the matrix apparatus. A stream of argon ($2\ mmol\,h^{-1}$) was directed over the sample held at 173 K, and the resulting gas mixture was condensed onto the mirror plane of a rhodium-plated copper support held at 15 K. Photolysis experiments were performed with a high-pressure mercury lamp (TQ 150, Heraeus) using a water-cooled quartz lens optic and cut-off filters (Schott). Details of the matrix apparatus are given elsewhere.[26] The IR spectra of the argon matrices were recorded in reflectance mode with a Bruker IFS 66v spectrometer using a transfer optic. A mercury cadmium telluride (MCT) detector and a KBr/Ge beam splitter were used in the wavenumber range 5000–650 cm^{-1}. For the spectra with apodized resolutions of 0.5 and 0.15 cm^{-1}m, 100 scans were added.

For the ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopic measurements, neat samples of $CH_3C(O)SeH$ and $CD_3C(O)SeD$ were held in flame-sealed, thin-walled 4 mm tubes, which were placed inside 5 mm NMR tubes. The spectra were recorded with a Bruker Avance 250 spectrometer operating at 250.13, 62.90, or 47.72 MHz for the ^{1}H, ^{13}C, and ^{77}Se NMR spectra, respectively. The samples were held at 243 K, and CD_3OD was used as an external lock and reference.

UV/Vis spectra of gaseous samples of $CH_3C(O)SeH$ and $CD_3C(O)SeD$ were recorded using a glass cell (optical path length 10 cm) equipped with quartz windows placed in the sample compartment of a Lambda 900 spectrometer (Perkin–Elmer, Norwalk, CT). The measurements were carried out in the spectral range 200–500 nm.

X-ray diffraction: An appropriate crystal of $CH_3C(O)SeH$ was grown in a capillary on a Siemens SMART-CCD diffractometer (Mo Kα radiation) at 143(2) K employing a miniature zone-melting procedure using an automated device with focused infrared laser radiation.[27] Cell dimensions $a = 10.212(2)$, $b = 11.741(2)$, $c = 6.8652(10)$ Å, $V = 823.1(2)$ Å^3, orthorhombic, $Z = 8$, 862 independent and 568 observed reflections, structure solved with direct methods and refined with the program SHELXTL-Plus,[28] 49 parameters, $R1 = 0.0475$, $wR2 = 0.1126$.

All quantum-chemical calculations were performed with the Gaussian 03 program package.[29] Second-order Møller–Plesset (MP2) and density-functional B3LYP methods were employed using different basis sets. Geometries were optimized by standard gradient techniques with simultaneous relaxation of all geometric parameters. Wavenumbers of vibrational modes were calculated for the optimized geometry for which no imaginary vibrational wavenumbers were found. The IR spectra calculated for $CH_3C(O)SeH$ and $CD_3C(O)SeD$, and those observed for the matrix-isolated molecules are presented in Figures S11 and S12 in the Supporting Information.

Received: July 19, 2008
Published online: November 17, 2008

Keywords: chalcogenocarboxylic acids · selenium · selenoacetic acid · vibrational spectroscopy

[1] S. Kato, H. Kageyama, K. Takaci, K. Mizoguchi, T. Murai, *J. Prakt. Chem.* **1990**, *332*, 898–910.
[2] Y. Kojima, K. Ibi, T. Kanda, H. Ishihara, T. Murai, S. Kato, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 990–992.
[3] Y. Kawahara, S. Kato, T. Kanda, T. Murai, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1881–1885.
[4] H. Kageyama, T. Murai. T. Kanda, S. Kato, *J. Am. Chem. Soc.* **1994**, *116*, 2195–2196.
[5] S. Kato, Y. Kawahara, H. Kageyama, R. Yamada, O. Niyomura, T. Murai, T. Kanda, *J. Am. Chem. Soc.* **1996**, *118*, 1262–1267.
[6] E. D. Jemmis, K. T. Giju, J. Leszczynski, *J. Phys. Chem. A* **1997**, *101*, 7389–7395.
[7] D. A. Clabo, Jr., H. D. Dickson, T. L. Nelson, *J. Mol. Model.* **2000**, *6*, 341–348.
[8] Q. Li, G. Liang, X. Wang, S. Chu, Y. Ren, *Int. J. Quantum Chem.* **2007**, *107*, 921–929.
[9] A. Kekule, *Ann. Chem. Pharm.* **1854**, *90*, 309–311.
[10] a) J. C. Fitzmaurice, D. J. Willians, P. T. Wood, J. D. Woollins, *J. Chem. Soc. Chem. Commun.* **1988**, 741–743; b) P. Bhattacharyya, J. D. Woollins, *Tetrahedron Lett.* **2001**, *42*, 5949–5951; c) I. P. Gray, P. Bhattacharyya, A. M. Z. Slawin, J. D. Woollins, *Chem. Eur. J.* **2005**, *11*, 6221–6227.
[11] S. Knapp, E. Darout, *Org. Lett.* **2005**, *7*, 203–206.
[12] C. Reilly, *Selenium in Food and Health, 2nd ed.*, Springer, New York, **2006**.

[13] C. V. Berney, R. L. Redington, K. C. Lin, *J. Chem. Phys.* **1970**, *53*, 1714 – 1721.

[14] H. S. Randhawa, W. Walter, C. O. Méese, *J. Mol. Struct.* **1977**, *37*, 187 – 192.

[15] A. B. Harvey, M. K. Wilson, *J. Chem. Phys.* **1966**, *45*, 678 – 688.

[16] D. M. Cameron, W. C. Sears, H. H. Nielsen, *J. Chem. Phys.* **1939**, *7*, 994 – 1002.

[17] H. H. Jaffé, M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, Wiley, New York, **1966**.

[18] S. Nagata, T. Yamabe, K. Fukui, *J. Phys. Chem.* **1975**, *79*, 2335 – 2340.

[19] O. Niyomura, S. Kato, *Chalcogenocarboxylic Acids*, Springer, Heidelberg, **2005**, pp. 5 – 6.

[20] H. Dubost, *Chem. Phys.* **1976**, *12*, 139 – 151.

[21] R. M. Romano, C. O. Della Védova, A. J. Downs, *J. Phys. Chem. A* **2002**, *106*, 7235 – 7244.

[22] R. A. Hill, T. H. Edwards, *J. Chem. Phys.* **1965**, *42*, 1391 – 1396.

[23] J. A. Gómez, R. M. Romano, unpublished results.

[24] A. Cabana, G. B. Savitsky, D. F. Hornig, *J. Chem. Phys.* **1963**, *39*, 2942 – 2950.

[25] H. Beckers, Y. S. Kim, H. Willner, *Inorg. Chem.* **2008**, *47*, 1693 – 1696.

[26] H. Schnöckel, H. Willner in *Infrared and Raman Spectroscopy, Methods and Applications* (Ed.: B. Schrader), VCH, Weinheim, **1994**, p. 297.

[27] R. Boese, M. Nussbaumer, *In situ Crystallization Techniques In Organic Crystal Chemistry* (Ed.: D. W. Jones), Oxford University Press, Oxford, **1994**, pp. 20 – 37.

[28] SHELTX-Plus, A Complex Software Package for Solving, Refining and Displaying Crystal Structures, version SGI IRIS Indigo, Siemens, Munich, Germany, **1991**.

[29] Gaussian 03 (Revision D.01), M. J. Frisch et al., Gaussian, Inc., Pittsburgh, PA, **2003**; see the Supporting Information.