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^{77}Se Chemical Shift Tensor of L-selenocystine: Experimental NMR Measurements and Quantum Chemical Investigations of Structural Effects

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Abstract

The genetically encoded amino acid selenocysteine and its dimeric form, selenocystine, are both utilized by nature. They are found in active sites of selenoproteins, enzymes that facilitate a diverse range of reactions, including the detoxification of reactive oxygen species and regulation of redox pathways. Due to selenocysteine and selenocystine's specialized biological roles, it is of interest to examine their ^{77}Se NMR properties and how those can in turn be employed to study biological systems. We report the solid-state ^{77}Se NMR measurements of the L-selenocystine chemical shift tensor, which provides the first experimental chemical shift tensor information of selenocysteine-containing systems. Quantum chemical calculations of L-selenocystine models were performed to help understand various structural effects on ^{77}Se L-selenocystine's chemical shift tensor. The effects of protonation state, protein environment, and substituent of selenium-bonded carbon on the isotropic chemical shift were found to be in a range of ca. 10–20 ppm. However, the conformational effect was found to be much larger, spanning ca. 600 ppm for the C-Se-Se-C dihedral angle range of -180° to $+180^\circ$. Our calculations show that around the minimum energy structure with a C-Se-Se-C dihedral angle of ca. -90° , the energy costs to alter the dihedral angle in the range from -120° to -60° are within only 2.5 kcal/mol. This makes it possible to realize these conformations in a protein or crystal environment. ^{77}Se NMR was found to be a sensitive probe to such changes and has an isotropic chemical shift range of 272 ± 30 ppm for this energetically favorable conformation range. The energy-minimized structures exhibited calculated isotropic shifts that lay within 3–9% of those reported in previous solution NMR studies. The experimental solid-state NMR isotropic chemical shift is near the lower bound of this calculated range for these readily accessible conformations. These results suggest that, the dihedral information may be deduced for a protein with appropriate structural models. These first-time

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Author Contributions

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experimental and theoretical results will facilitate future NMR studies of selenium-containing compounds and proteins.

Introduction

Selenium lies directly below sulfur on the periodic table and, thus, shares with it many physicochemical properties.¹ The health benefits of selenium are attributed to its presence in selenoproteins, a class of enzymes involved in multiple disorders such as cancer, inflammation, and neurodegenerative diseases.² Selenocysteine is specifically incorporated into genetically encoded positions by reading the UGA codon,³ and it is central to selenoproteins' high reactivity.⁴ In selenoproteins selenocysteine is either unconjugated, bound to a thiol such as cysteine or glutathione,⁵ or found in the dimeric form selenocystine that contains a diselenide bond.^{6–8} How these forms are activated by the protein environment and take part in enzymatic reactions is the focus of intense research.^{4, 9}

In addition to selenocysteine and selenocystine's important roles in human health, there is also interest in engineering novel selenoproteins with diselenide bonds to either promote the proper connectivity in a given protein during folding (the process of oxidative protein folding)¹⁰ or to generate stable proteins that can be beneficial for biomedical applications.¹¹ Selenocystine itself is being examined for potentiating cancer therapy. Success in these endeavors rests on a detailed understanding of the chemical and physical properties of the diselenide bond.^{12–13} In order to provide insights and open avenues for further studies we determine here the solid-state NMR characteristics of L-selenocystine ⁷⁷Se.

⁷⁷Se is highly sensitive to its local environment, with a chemical shift range spanning almost 6000 ppm.^{14–16} It has been employed previously in solution-state NMR studies to report the chemical properties of selenocystine in its free form^{17–19} as well as incorporated in peptides and proteins.^{20–24} However, the full information about the ⁷⁷Se response to its environment in selenocysteine and selenocystine, that is the chemical shift tensor, has not yet been reported. This limited data may be a result of the fact that the two compounds have limited solubility at physiological pH^{25–26} and tend to undergo elimination and oxidation reactions.²⁷ Furthermore, while theoretical calculations of the ⁷⁷Se chemical shielding tensor were reported, they were only analyzed in terms of isotropic shifts due to an absence of data about selenocysteine and selenocystine chemical shift tensor.²⁴ Here we report the ⁷⁷Se chemical shift tensor of L-selenocystine recorded by ⁷⁷Se cross-polarization magic angle spinning (CP/MAS) solid-state NMR (SSNMR).

In addition to the experimental measurements of selenocystine ⁷⁷Se chemical shift tensor, we also describe theoretical investigations of various structural effects on the chemical shielding tensor of selenocystine. Calculations of selenium magnetic shielding tensors have been increasingly improving in accuracy,²⁸ and for small organoselenium compounds they yield close agreement (5–30%) with experiments.^{29–31} Isotropic chemical shifts for selenoproteins and selenol amino acids as well as magnetic shielding tensors of bioactive selenium compounds have also been numerically assessed³² and found to be in relatively good agreement with experimental data (ca. 15%).^{33–34} Density functional theory (DFT) calculations have proven to be instrumental to understanding the local environment of

selenocysteine in selenoproteins.²⁴ However, in that work only the isotropic chemical shifts of selected isomers were experimentally measured and available for comparison. Furthermore, there is not yet a systematic survey of the influence of structural effects on ⁷⁷Se chemical shielding tensor. Therefore, calculations of various selenocysteine models were used to explore the effect of different kinds of structural parameters on the ⁷⁷Se chemical shift tensor to provide useful information for future ⁷⁷Se NMR studies of biological systems.³⁵

Materials and Methods

All reagents and solvents were of the highest purity grade. L-selenocystine (98% purity) was purchased from Acros Organics and used without further purification. According to the manufacturer, L-selenocystine was synthesized by coupling 3-chloro-L-alanine with disodium diselenide.^{36–37} The obtained product was dissolved in 1 N HCl and crystallized as L-selenocystine after neutralization with 6N NaOH.

Data acquisition and analysis

Spectra were acquired on a 500WB Bruker AV3 spectrometer using a 4 mm CP/MAS probe with 40 mg sample in a 4 mm rotor. Each spectrum has 2048 data points, a contact time of 2 ms, and a spectral width of 100 kHz. Depending on sample rotation rate, between 1024 and 16384 transients were accumulated using a recycling delay of 2.5 s. During the cross polarization a 70 kHz spinlock was employed to the ⁷⁷Se nuclei with a 20% amplitude ramp on the ¹H nuclei at the n+1 condition. During acquisition 100 kHz SPINAL64³⁸ heteronuclear decoupling on ¹H was applied. Spectra were processed with a 300 Hz Gaussian apodization function. Unless otherwise noted data were acquired at 261 K. Temperature calibration was performed using KBr.³⁹ Spectra were referenced using ammonium selenate as a secondary chemical shift reference standard, set at 1040.2 ppm, while dimethyl selenide was employed as primary reference at 0 ppm.¹⁴ The chemical shift tensor was calculated from the spectra using the program SOLA by BRUKER.

Theoretical methods

DFT calculations were performed with the program Gaussian 09.⁴⁰ Geometry optimizations were done using the mPW1PW91 method⁴¹ based on its excellent performance in previous computational work on molecules containing elements in 4th and later periods,^{42–47} including the computational ⁷⁷Se NMR study.³⁴ For NMR chemical shielding tensor calculations, both mPW1PW91 and a recently developed DFT method ωB97XD⁴⁸ which includes dispersion correction were examined, using the default gauge-independent atomic orbital (GIAO) method implemented in Gaussian 09. Both the widely used NMR computational basis set 6-311++G(2d,2p)⁴⁹ and the all electron Huzinaga basis set 14s10p5d⁵⁰ were investigated in the current work. In some calculations, solvent effects were also examined using the default polarization continuum method (PCM) in Gaussian 09.⁵¹

Results and Discussion

Experimental solid-state ^{77}Se NMR measurements

We have recorded the chemical shift tensor of L-selenocystine by ^1H - ^{77}Se CP/MAS. The spectra of L-selenocystine, acquired at different spinning speeds ranging from 1.5 to 10 kHz at 261 K, are presented in Figure 1. Only one selenium environment is evident. The calculated values for the chemical shielding parameters (87% overlap) are $\delta_{11}=482.5$ ppm, $\delta_{22}=350.5$ ppm, $\delta_{33}=-119.0$ ppm, $\delta_{\text{iso}}=238.1$ ppm, in Herzfeld-Berger notation,⁵² $\Omega=601.5$ ppm, $k=0.56$, Haeberlen notation: $d=-357.0$ ppm and $h=0.37$ for the CP/MAS results with 5 kHz sample rotation, with a sample temperature of 261 K (Figure 2). These values agree well with reported selenium chemical shift tensors in diselenide bonds of organic molecules whose span range between 500 and 900 ppm.¹⁵

We next examined the effect of molecular motion by conducting experiments at variable temperatures over a range of 210 to 340 K (Figure 3). There is no experimental evidence for dynamical processes influencing the measurements. Fitting the spectra acquired at 217 K, we find that the isotropic chemical shift moved by 3 ppm compared to its position at 261 K. All other parameters of the anisotropic chemical shift, span, and anisotropy do not change measurably. The isotropic chemical shift at 323 K was found to be 242 ppm, which indicates a gradient of approximately 0.067 ppm/K. The observed changes in isotropic chemical shifts are comparable to reported temperature induced changes in spectra of diselenides.¹⁴

Theoretical study of structural effects on NMR properties

The experimental isotropic chemical shift reported here has a difference of close to 60 ppm from that recorded by solution NMR.¹⁷ That raises the possibility that in the solid form, the crystal packing or intermolecular interactions in the solid state may cause some structural changes compared to the solution state. Our attempts to crystallize L-selenocystine under inert atmosphere, following published procedures for L-cystine crystallization,^{53–56} did not lead to diffraction quality crystals. Thus, the crystal X-ray structure of selenocystine could not be determined at this point.

In the absence of detailed geometric information regarding crystalline selenocystine, we undertook calculations of the magnetic shielding tensor with a particular focus on structural effects. A number of structural models were examined to reveal details of the structural sensitivity of the ^{77}Se chemical shift tensor. First, the small MeSeSeMe compound was used to fine tune our methodological approach for calculating the chemical shielding tensor of molecules with a diselenide bond. These calculations were referenced using the Me_2Se as standard. The isotropic chemical shift, δ_{iso} , for MeSeSeMe in chloroform has been measured to be 274 ppm on average (see Table 1 of ref ³⁴). Earlier calculations using the mPW1PW91 method and several different basis sets yielded consistent good predictions of shifts in the range from 289 to 291 ppm.¹⁴ The same mPW1PW91 method but with a 6-31+G(2d) basis set for all atoms was employed here for geometry optimization. It has been previously found that this approach yielded excellent predictions of geometric parameters in large, biologically relevant systems.⁴⁴ To calculate the NMR properties, a 6-311++G(2d,2p) basis set for all atoms was utilized. Solvent effects were included in both geometry optimization

and subsequent NMR calculations, which produced a similarly good prediction of 289 ppm. Further improvement was found with a recently developed DFT method with dispersion correction, ω B97XD, which predicted an isotropic shift of 271 ppm and thus an error of only 3 ppm or 1%. This is consistent with its improved performance compared to mPW1PW91 as reported in a recent NMR chemical shielding study.⁵⁷ In addition, the impact of the choice of the basis set on the NMR calculation was investigated. Using the all electron Huzinaga basis set⁵⁰ 14s10p5d, calculations with ω B97XD resulted in an isotropic chemical shift of 299 ppm. The comparatively large deviation from the experimental value was somewhat surprising as the same approach resulted in a good agreement with the experimentally determined nuclear magnetic shielding tensor in previous work on Se-N heterocycles.³⁰ Based on these results, it was deemed appropriate to use mPW1PW91/6-31+G(2d) in geometry optimization and ω B97XD/6-311++G(2d,2p) for all subsequent NMR calculations.

As the crystal structure of selenocystine is unavailable, structural models were initially constructed using high-resolution X-ray structures of L-cystine. The zwitterion form, crystallized in a P6122 space group symmetry with an R factor of 1.4,⁵⁶ is entry LCRYSTI14 in the Cambridge Crystallographic Data Centre (CCDC). The positively charged L-cystine, in the presence of chlorine (i.e. both the amino and carboxyl groups are protonated), crystallized in a C2 space group with an R factor of 1.78 is entry CYSTCL03 in the CCDC.⁵⁸ In the solid form, the terminal charged groups are usually involved in electrostatic/hydrogen bonding, as evidenced in selenomethionine's X-ray structures.^{59–60} This interaction has an effect similar to charge neutralization. Therefore, single molecular models with partially charged amino or carboxylate terminal groups may be reasonably good approximations for the crystal form of selenocystine.

As shown in Table 1, several models were investigated here with corresponding optimized structures shown in Figure 4. The Se-Se bond length ranged from 2.32 to 2.33 Å in the optimized geometries of these models. The optimized diselenide bond lengths are in good agreement with a survey of the distribution of diselenide bond length in the CCDC with a mean of 2.36 Å and a median of 2.34 Å. The Sec-Sec-1 model is based on the L-cystine structure CYSTCL03 with the sulfur replaced by selenium and full optimization in the gas phase. It is interesting to note that although the predicted δ_{iso} of 312 ppm is ca. 30% off from the solid-state NMR measurement, it is within 6% error of the solution NMR result of 294 ppm for L,L-(⁷⁷Se)-selenocystine.¹⁶ This suggests that the optimized structure may be more closely related to the conformation in the solution phase than in the solid state. The Sec-Sec-2 model was then used to investigate the environmental effect. In contrast to the Sec-Sec-1 model, the Sec-Sec-2 model was optimized with an implicit solvent model to mimic the dielectric environment. A dielectric constant of 10 based on a previous study of NMR shift calculations of dipeptides was employed.⁶¹ The use of a dielectric environment is a common practice to simulate the effect of the protein environment. As shown in Table 1, the medium effect is 10 ppm, which means the predicted δ_{iso} deviates by only 3% from the solution value.¹⁷ The error reduction on the isotropic chemical shift for solid state NMR δ_{iso} is 3%, while the error on the span was improved by 11%. This suggests that the medium effect may be used to improve predictions of solid-state NMR results. However, the

computational result for the chemical shielding tensor of this single molecular model still deviates significantly from the solid-state experimental data.

As was shown in a previous study,⁶² additional improvement on the prediction accuracy of the chemical shift tensor requires sophisticated models that include both the information from X-ray crystal structure of the molecule of interest and its environmental effects. Although that vital information is currently not available, the excellent accuracy with errors of 1–3% for solution ⁷⁷Se NMR results for MeSeSeMe and selenocystine provides a solid basis for the calculations to probe structural effects for future studies.

To investigate the effect of protonation state, the Sec-Sec-3 model was used. Compared to Sec-Sec-1, the difference is that the initial protonation state setup of Sec-Sec-3 is a zwitterionic form. In the absence of stabilizing intermolecular interactions usually present in crystal structures or protein environments, a proton was transferred from the amino group to the carboxylate group during the optimization, as shown in Figure 4C, leading to a neutralized model. Although the final Sec-Sec-3 structure compared to Sec-Sec-1 lacks the extra positively charged protons, the resulting δ_{iso} is only different by 7 ppm from that of the Sec-Sec-1 model, indicating that the protonation state has a minor effect (~2%).

EtSeSeEt was studied to further investigate the effects of terminal groups in selenocystine. As seen from Table 1, this substituent effect is larger than the protonation state effect. It resulted in a 20 ppm difference when compared to the δ_{iso} of the neutral Sec-Sec-3 model. Furthermore, the spans were different by 191 ppm. Overall, the effects of protonation state, protein environment, and substituent of selenium-bonded carbon were found to be in a range of ca. 10–20 ppm for the isotropic shift. This is consistent with the rather small range of the C-Se-Se-C dihedral angles of -88° to -94° as seen in the models of Sec-Sec-1, Sec-Sec-3, and EtSeSeEt (Table 1).

It should be noted that in all above models, the C-Se-Se-C dihedral angle is negative and thus similar to the dihedral angle in L-cystine X-ray structure of the positively charged form. Thus, we next studied the neutral L-cystine form, LCYSTI14, with a positive dihedral angle, by changing the dihedral angle in Sec-Sec-3 model to that of LCYSTI14 and then minimizing the whole molecule. The resulting C-Se-Se-C dihedral angle of the optimized structure (model Sec-Sec-4) is 68° . The calculated δ_{iso} of this structure, 144 ppm, has the largest difference from the values measured by both solid- and solution-phase NMR among all models used here. This suggests that the conformational effect is larger than other structural effects studied above. A correlation between the R'-Se'-Se-R dihedral angle and the ⁷⁷Se NMR properties was previously found experimentally in organic diselenides.^{63–64} Yet, to our knowledge, there are no prior experimental or theoretical studies of such relationships in selenocystine. To investigate this effect in more detail, we used the Sec-Sec-2 model because it exhibited the smallest error relative to the solution NMR shift (3%), and calculated corresponding NMR chemical shielding properties when varying the C-Se-Se-C dihedral angle in the range from -180° to $+180^\circ$. As shown in Table 2 and Figure 5, this resulted in a much larger change in δ_{iso} values (614 ppm) compared to other structural effects studied here. Of the shift tensor elements, δ_{11} and δ_{22} are most affected, both with a range of 679 ppm, while the range for δ_{33} is only 247 ppm. As seen from Figure 5A–D, the

trend of δ_{22} is most similar to that of δ_{iso} . In fact, the linear correlation coefficient between these two properties (R^2) is 0.915. The energy diagram in Figure 5E shows that the optimized structure with a near -90° C-Se-Se-C angle is indeed the energy minimum for angles between -180° and $+180^\circ$. Conformations of $\pm 30^\circ$ around this minimum only entail <2.5 kcal/mol energy costs. This indicates that when selenocystine is in the solid form or part of a protein, the intermolecular or environmental effect may easily overcome this small energy barrier and lead to altered conformations. Interestingly, although our current solid-state NMR isotropic shift is ca. 20% lower than that from the solution measurement, a conformation of -120° with only 2.23 kcal/mol energy cost has a δ_{iso} of 242 ppm (see Table 2), which is only a 4 ppm (1.7%) difference from our solid-state experimental measurement. The skew for this conformation, 0.43, is also close to our experimental solid-state NMR result of 0.56. Clearly, these calculations show that conformational details have a significant effect on ^{77}Se NMR properties.

Conclusions

In summary, we report the measurements of selenocystine chemical shift tensor and its temperature dependence. This constitutes to the best of our knowledge the first experimental chemical shift tensor information of selenocystine-containing systems. It illustrates that the environmental effect, such as crystal packing, can affect ^{77}Se NMR properties appreciably as exemplified by the 20% difference between the isotropic shift recorded by solid-state NMR versus the shifts recorded by solution NMR. Numerous selenocystine models were investigated theoretically to help understand various structural effects on the ^{77}Se NMR chemical shift tensor of selenocystine. The calculations for both MeSeSeMe and selenocystine are within 1–3% error compared to the solution NMR values. The effects of protonation state, protein environment, and substituent of selenium-bonded carbon were found to be relatively small with a range of ca. 10–20 ppm (3%–8%) for the isotropic shift. The most significant effect studied here is the conformation, reflected by a change of over 600 ppm for the isotropic shift as the dihedral angle for C-Se-Se-C is varied between -180° and $+180^\circ$. The significant contribution of the local bonding environment, specifically the diselenide dihedral angle, to calculations of ^{77}Se NMR parameters was previously reported.^{31,63–64} Griffin and coworkers demonstrated the large influence of the torsion angles that define the diselenide linkage to theoretically calculated isotropic chemical shieldings in some non-biological samples. Our studies reinforce this conclusion for the case of selenocystine, in addition to unprecedented evaluations of the torsion effect on magnetic shielding tensors and associated energies, as well as contributions quantitatively relative to those from other kinds of structural effects. Our calculations show that it only takes less than 2.5 kcal/mol of energy to alter the dihedral angle by as much as 30° around the energy minimum conformation (ca. -90°). These results suggest that in a protein or crystal environment, selenocystine's conformation could vary significantly from the ideal values seen for optimized small model molecules and that ^{77}Se NMR can be a sensitive technique to probe details of molecular structures. For instance, the $-90 \pm 30^\circ$ conformations have an isotropic shift range of 272 ± 30 ppm, with the current solid-state ^{77}Se NMR isotropic shift being near the lower bound of this range. Therefore, it is likely that the dihedral angle of the diselenide (and by extension the selenylsulfide bond) in proteins may be deduced from

experimental data by using appropriate structural models in concert with a detailed conformational map of ^{77}Se NMR shifts as exemplified in Figure 5. Thus, these initial experimental and theoretical results will facilitate future analysis of NMR studies of selenocysteine-containing compounds and proteins.

In analogy to cysteine-containing proteins, the geometry and environment of selenocysteine and selenocysteine in selenoproteins is likely to shape their ability to act as a nucleophile and thus impact their reactivity.^{65–66} To understand this connection in detail, it is of great interest to extend the NMR studies presented here to additional biological systems.

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ABBREVIATIONS

SSNMR	solid-state NMR
DFT	Density Functional Theory
GIAO	gauge-independent atomic orbital
CP/MAS	cross-polarization magic angle spinning

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Figure 1. ^{77}Se SSNMR of selenocystine. ^{77}Se - ^1H variable-amplitude cross polarization magic angle spinning spectra at different spinning speeds ranging from 1.5 to 10 kHz, acquired at 11.75 T.

Figure 2. Experimental and calculated spectrum of selenocystine. Experimental (bottom) and best-fitting (top) simulated spinning chemical shift anisotropy sideband pattern for selenocystine. The experimental spectrum was recorded at 11.75 T, a temperature of 261 K, and a spinning rate of 5 kHz.

Figure 3.

Temperature dependence of selenocystine shielding parameters. ^{77}Se - ^1H variable-angle cross-polarization magic angle spinning spectra of selenocystine at 261 K (lower spectrum) and at 216 K (upper spectrum) at 5 kHz sample rotation rate, acquired at 11.75 T.

Figure 4. Models of the selenocystine structures used for DFT calculations. A) Sec-Sec-1; B) Sec-Sec-2; C) Sec-Sec-3; D) Sec-Sec-4.

Figure 5.
The dependence of key NMR parameters and energies on the torsion angle C-Se-Se-C. A) δ_{iso} ; B) δ_{11} ; C) δ_{22} ; D) δ_{33} ; E) ΔE .

Table 1
Computational results of principle components of the chemical shift tensor for L-selenocystine models.

Models	$\angle \text{C-Se-Se-C} (^{\circ})$	$R_{\text{SeSe}} (\text{\AA})$	$\delta_{\text{iso}} (\text{ppm})$	$\delta_{11} (\text{ppm})$	$\delta_{22} (\text{ppm})$	$\delta_{33} (\text{ppm})$	$\Omega (\text{ppm})$	κ
Sec-Sec-1	-93.6	2.33	312	658	576	-297	955	0.83
Sec-Sec-2	-92.9	2.32	302	612	570	-276	888	0.91
Sec-Sec-3	-88.3	2.33	319	668	487	-197	865	0.58
EtSeSeEt	-89.1	2.32	339	579	532	-95	674	0.86
Sec-Sec-4	67.9	2.33	144	563	244	-374	937	0.32

Table 2

Computational results of conformational effect on principle components of the chemical shift tensor for L-selenocystine model Sec-Sec-2.

$\angle\text{C-Se-C } (^{\circ})$	δ_{iso} (ppm)	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)	Ω (ppm)	κ	E (kcal/mol)
-180	29	605	-73	-445	1050	-0.29	9.44
-140	157	670	167	-364	1034	0.03	5.18
-120	242	667	385	-328	995	0.43	2.23
-110	274	644	484	-306	950	0.66	1.24
-100	295	606	568	-287	893	0.92	0.27
-95	302	602	580	-277	879	0.95	0.02
-93	302	612	570	-276	888	0.91	0.00
-90	303	629	551	-271	900	0.83	0.03
-85	301	652	518	-266	918	0.71	0.11
-80	298	671	481	-257	928	0.59	0.27
-70	280	691	398	-249	940	0.38	1.08
-60	247	684	307	-251	935	0.19	2.44
-40	134	572	121	-290	862	-0.05	7.05
-20	-22	327	-27	-365	692	-0.02	17.05
0	-100	184	-95	-388	572	0.03	26.08
20	12	368	2	-335	703	-0.04	22.43
40	182	567	231	-251	818	0.18	21.00
60	318	701	454	-202	903	0.45	23.14
70	364	757	534	-198	955	0.53	23.10
80	386	790	578	-211	1001	0.58	22.15
85	387	797	584	-221	1018	0.58	21.89
90	381	798	577	-233	1031	0.57	21.55
95	368	795	556	-247	1042	0.54	20.90
100	350	791	522	-262	1053	0.49	19.80
110	308	782	427	-284	1066	0.33	17.38
120	257	765	315	-308	1073	0.16	14.84

$\angle \text{C-Se-C } (^{\circ})$	δ_{iso} (ppm)	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)	Ω (ppm)	κ	E (kcal/mol)
140	149	704	95	-352	1056	-0.15	10.87
180	29	605	-73	-445	1050	-0.29	9.44