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Structures and Vibrational Spectroscopic Parameters of Selenoxopropanedinitrile and Selenoxosilanedicarbonitrile: Theoretical Study Based on Density Functional Theory Method

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ABSTRACT: *The molecular structures and vibrational spectra in harmonic and anharmonic approximations have been studied for selenoxopropanedinitrile and selenoxosilanedicarbonitrile in the gas phase. Density functional theory method with B3LYP functional and cc-pVTZ basis set has been employed. Optimized structural parameters and spectroscopic constants, namely, anharmonic, rotational and centrifugal distortion, rotation–vibration coupling, and Coriolis coupling parameters, are reported. Infrared vibrational and Raman frequencies are provided with complete assignments to the fundamental bands, overtones, and combination tones of the molecules. This study shows that silicon for carbon substitution affects mainly those properties that are dependent on the C=Se bond. The literature for these molecules is not available and therefore the data from this work would be suitable for their characterizations as and when they are synthesized.* Heteroatom Chem 20:208–217, 2009; DOI 10.1002/hc.20535

INTRODUCTION

Oxopropanedinitrile ($O{=}C(C{\equiv}N)_2$) is an interesting compound because of the combination of the carbonyl and nitrile functional groups. It has been the subject of several experimental [1–7] and theoretical studies [8,9]. In 1971, Tyrrell and coworkers [3] reported the experimental infrared and Raman spectra for oxopropanedinitrile. The 12 fundamental frequencies of the molecule were assigned. In 1991, Tyrrell and coworkers [3] reported ab initio calculations using 6-31G(d) basis sets at the MP2 level and the calculated geometries and frequencies compare well with experimental data. More recently, in 2006, Gupta and Sharma [9] attempted a detailed analysis of the vibrational spectra of oxopropanedinitrile in harmonic and anharmonic approximations. There have been attempts to explore the sulfur analogue [8] of oxopropanedinitrile. However, to the best of our knowledge, no studies have been done for the selenium analogue, namely, selenoxopropanedinitrile ($Se{=}C(C{\equiv}N)_2$), although the effect of sulfur and selenium for oxygen substitution has been investigated for other compounds [10–12]. This is also surprising because there are increasing possibilities for the synthesis of the sulfur, selenium, and even tellurium analogues of carbonyl compounds [13,14]. Very recently, Xu et al. [15] reported the biosynthesis of selenocysteine on its *t*RNA in eukaryotes and the selenium-containing amino acid is recognized to be the 21st amino acid in the genetic code. More interestingly, they found that the selenium in

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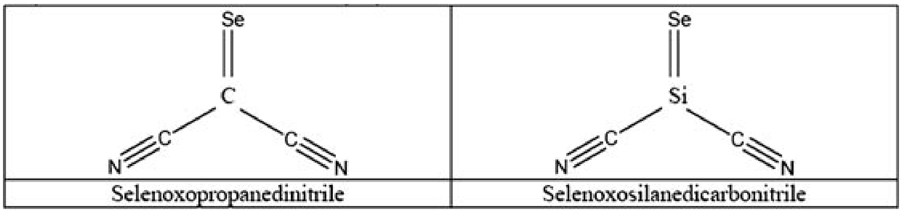


FIGURE 1 C_{2v} structures of selenoxopropanedinitrile and selenoxosilanedicarbonitrile.

selenocysteine is believed to play an essential protective role in the body, including preventing cancer and heart diseases and delaying aging. To address the deficiency of selenium analogue of oxopropanedinitrile and, in continuation with previous studies, selenoxopropanedinitrile has been the target of this study.

TABLE 2 Natural Charges (*e*) of Selenoxopropanedinitrile and Selenoxosilanedicarbonitrile

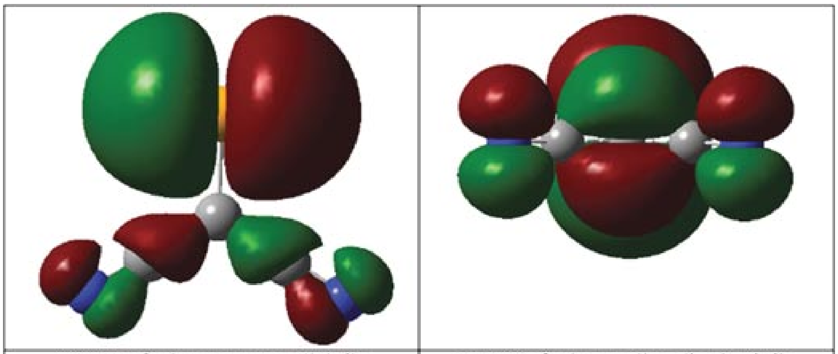
Selenoxopropanedinitrile		*Selenoxosilanedicarbonitrile*	
Se	0.3487	Se	−0.3124
C_{Se}	−0.3854	Si	1.1181
C_N	0.2217	C	−0.2036
N	−0.2034	N	−0.1992

On the basis of the so-called double-bond rule [16], it was accepted that compounds having a double bond between the heavier group 14 and 16 elements could not be synthesized. However, this is no more valid in its original formulation and it is more appropriate to state that these elements have lower tendency to form double bonds than the second-row elements. Su and coworkers [17] shed more light on this area by examining the effects of substituents on the stabilization of the double bond between silicon and selenium atoms. The potential energy surfaces of $X_2Si{=}Se$ ($X = H$, F, Cl, Br, SiH_3, and CH_3) were investigated by using B3LYP and QCISD(T) methods. They concluded that either electronegative or steric effects play a dominant role in determining the relative stability of $X_2Si{=}Se$ and XSi-SeX. In the context of this study, once selenoxopropanedinitrile has been targeted, it becomes appropriate to extend the study to include selenoxosilanedicarbonitrile ($Se{=}Si(C{\equiv}N)_2$).

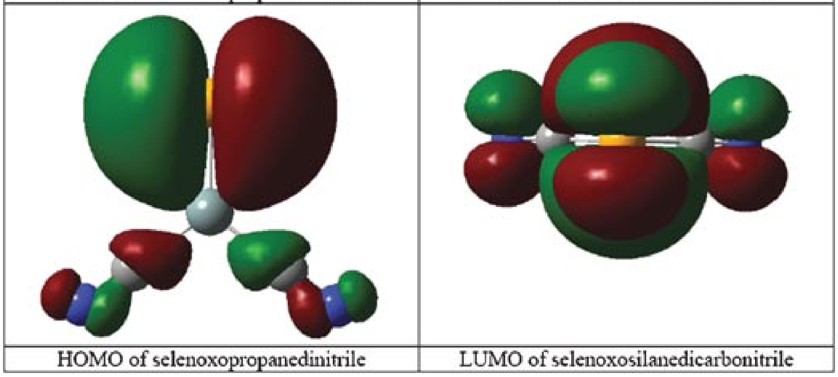
TABLE 1 Optimized Structural Parameters, Energies, Dissociation Energies, and HOMO–LUMO Gaps of Selenoxopropanedinitrile and Selenoxosilanedicarbonitrile

	Selenoxopropanedinitrile			*Selenoxosilanedicarbonitrile*	
	B3LYP	*MP2*		*B3LYP*	*MP2*
r (C=Se) (Å)	1.7818	1.7742	*r* (Si=Se) (Å)	2.0711	2.0605
r (C—C) (Å)	1.4214	1.4267	*r* (C—Si) (Å)	1.8291	1.8274
r (C≡N) (Å)	1.1543	1.1764	*r* (C≡N) (Å)	1.1541	1.1777
∠(CCC) (°)	116.4	116.4	∠(CSiC) (°)	105.9	105.4
∠(CCSe) (°)	121.8	121.8	∠(CSiSe) (°)	127.0	127.3
μ (Debye)	2.6769	3.0695	μ (Debye)	1.7614	1.1689
I_A (GHz)	2.971	2.919	I_A (GHz)	2.375	2.372
I_B (GHz)	1.092	1.899	I_B (GHz)	1.234	1.229
I_C (GHz)	1.160	1.151	I_C (GHz)	0.812	0.810
Energy (hartree)	−2625.447809	−2623.427242	Energy (hartree)	−2876.921426	−2874.518025
Dissociation energy (kJ/mol)	2883.87	2953.97	Dissociation energy (kJ/mol)	2715.48	2787.96
HOMO–LUMO gap (kJ/mol)	246.27	863.82	HOMO–LUMO gap (kJ/mol)	333.83	902.33
μ (kJ/mol)	−623.61	−618.06	μ (kJ/mol)	−591.14	−565.09
η (kJ/mol)	123.14	431.91	η (kJ/mol)	166.92	451.17

Spectral analysis is a very important component in the identification of molecules. It is has been found that density functional theory (DFT) method using hybrid functionals such as B3LYP can give reasonably accurate values of fundamental frequencies and other vibrational parameters [18,19]. However, very recently, Meier [20] illustrated that the capabilities to calculate vibrational spectra have greatly improved. Although it is computationally expensive, better results and more parameters are obtained if vibrational calculations are done using anharmonic



HOMO of selenoxopropanedinitrile | LUMO of selenoxosilanedicarbonitrile



HOMO of selenoxopropanedinitrile | LUMO of selenoxosilanedicarbonitrile

FIGURE 2 HOMO and LUMO of selenoxopropanedinitrile and selenoxosilanedicarbonitrile.

approximation. Barone [19] reported that the use of anharmonic approximation leads to frequencies that do not require any scaling.

In the present work, the optimized molecular structures and vibrational spectra, in harmonic and anharmonic approximations, are presented for the novel compounds selenoxopropanedinitrile and selenoxosilanedicarbonitrile in the gas phase. The results obtained in this work are expected to be useful because one of the goals for this study originates from the literature of these compounds being nonexistent. The findings of this work are presented herein.

COMPUTATIONAL METHODS

All calculations were performed with Gaussian 03W [21] and visualizations were done with GaussView [22]. Selenoxopropanedinitrile and selenoxosilanedicarbonitrile (Fig. 1) were studied in C_{2v} symmetry in the gas phase. Geometry optimization was carried out by DFT with B3LYP as the functional and cc-pVTZ as the basis sets. Vibrational frequencies in harmonic and anharmonic approximations were obtained after optimizing the molecular geometry by the same level of theory and basis sets. The calculation of vibrational frequencies in the harmonic approximation is limited because molecular vibrations are not purely harmonic. So far, scaling factors [23] have been used to improve harmonic frequencies, although anharmonic approximation leads to better results.

When we consider an anharmonic oscillator, the potential energy between atoms may be written as

$$V = \frac{1}{2}\sum_{ij} f_{ij} S_i S_j + \frac{1}{6}\sum_{ijk} f_{ijk} S_i S_j S_k + \frac{1}{24}\sum_{ijkl} f_{ijkl} S_i S_j S_k S_l + \cdots \tag{1}$$

where $[S_i]$ is the displacement of internal coordinates and f_{ij}, f_{ijk}, and f_{ijkl} are the quadratic, cubic, and quartic force constants.

The energy of an anharmonic oscillator may be written as

$$E_{n_1,n_2,\ldots} = \sum_i \nu_{0i}\left(n_i + \frac{1}{2}\right) + \sum_{j,k,k\geq i} X_{ik}\left(n_i + \frac{1}{2}\right)\left(n_k + \frac{1}{2}\right) + \cdots \tag{2}$$

where $[X_{ij}]$ and $[X_{ik}]$ are the diagonal and nondiagonal anharmonicity constants.

TABLE 3 Vibrational Parameters of Fundamental Bands of Selenoxopropanedinitrile and Selenoxosilanedicarbonitrile[a]

Vibration	*Harmonic*	*Anharmonic*	*Intensity*	*Mode*	*Raman Activity*	*Depolar (P)*	*Depolar (U)*	*Assignment*
				Selenoxopropanedinitrile				
ν_1	2315.0	2269.1	8.8	A_1	370.3	0.10	0.19	C≡N stretch
ν_2	1090.3	1073.3	34.2	A_1	67.5	0.20	0.33	C=Se stretch
ν_3	619.5	609.9	1.6	A_1	1.1	0.04	0.08	C—C stretch
ν_4	492.1	490.3	0.8	A_1	18.5	0.09	0.17	C—C—C bend
ν_5	132.1	132.8	4.3	A_1	7.9	0.72	0.83	C—C≡N bend
ν_6	381.4	378.6	0	A_2	0.9	0.75	0.86	C—C≡N bend
ν_7	633.3	627.3	4.4	B_1	1.72	0.75	0.86	Se=C(C≡N)$_2$ bend
ν_8	207.7	207.4	12.4	B_1	0.002	0.75	0.86	C—C≡N bend
ν_9	2302.3	2292.1	21.7	B_2	307.2	0.75	0.86	C≡N stretch
ν_{10}	1172.0	1158.8	34.6	B_2	15.0	0.75	0.86	C—C stretch
ν_{11}	468.3	464.5	0.2	B_2	0.7	0.75	0.86	Se=C—C bend
ν_{12}	177.8	177.3	2.2	B_2	4.3	0.75	0.86	C—C≡N bend
				Selenoxosilanedicarbonitrile				
ν_1	2295.3	2268.5	30.9	A_1	274.4	0.10	0.18	C≡N stretch
ν_2	715.4	713.4	107.7	A_1	38.1	0.30	0.46	Si≡Se stretch
ν_3	434.7	425.1	0.3	A_1	9.1	0.16	0.27	Si—C stretch
ν_4	381.5	377.5	1.0	A_1	14.0	0.07	0.14	C—Si—C bend
ν_5	93.7	93.6	5.9	A_1	5.9	0.75	0.87	Si—C≡N bend
ν_6	256.8	254.3	0	A_2	2.7	0.75	0.86	Si—C≡N bend
ν_7	338.5	334.8	0.05	B_1	6.7	0.75	0.86	Se=Si(C≡N)$_2$ bend
ν_8	128.2	128.1	19.2	B_1	0.1	0.75	0.86	Si—C≡N bend
ν_9	2293.0	2266.2	70.6	B_2	169.2	0.75	0.86	C≡N stretch
ν_{10}	663.1	659.7	109.9	B_2	109.9	0.75	0.86	Si—C stretch
ν_{11}	319.7	317.3	0.005	B_2	0.6	0.75	0.86	Se=Si—C bend
ν_{12}	115.6	114.8	6.2	B_2	4.8	0.75	0.86	C—C≡N bend

[a] Frequency is in $\mathrm{cm^{-1}}$, Raman activity is in $\mathrm{Å^4/amu}$ and intensity in km/mol.

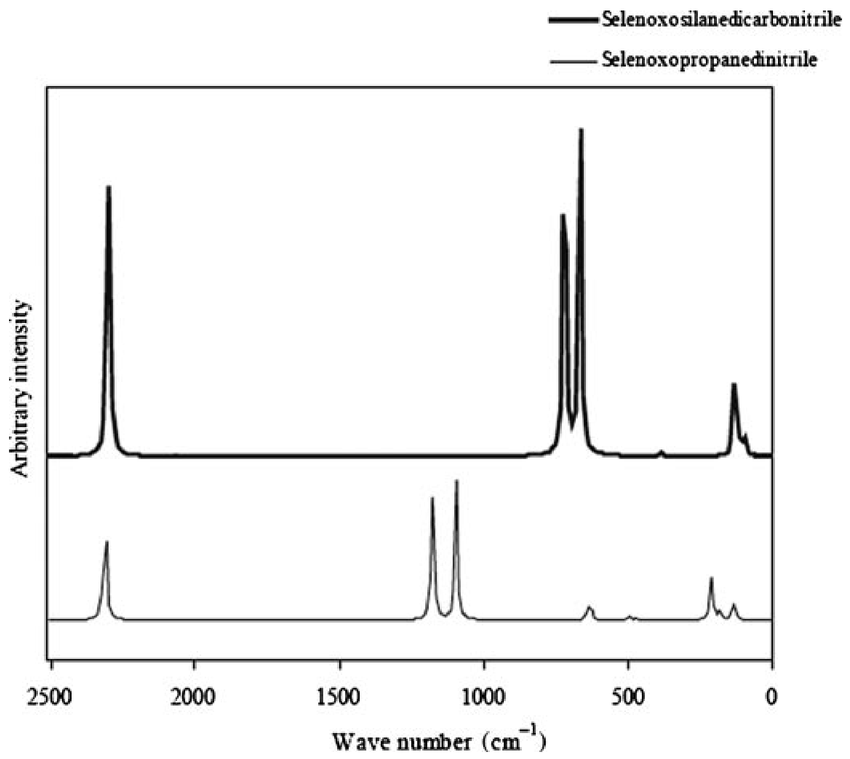


FIGURE 3 Simulated infrared spectra of selenoxopropanedinitrile and selenoxosilanedicarbonitrile.

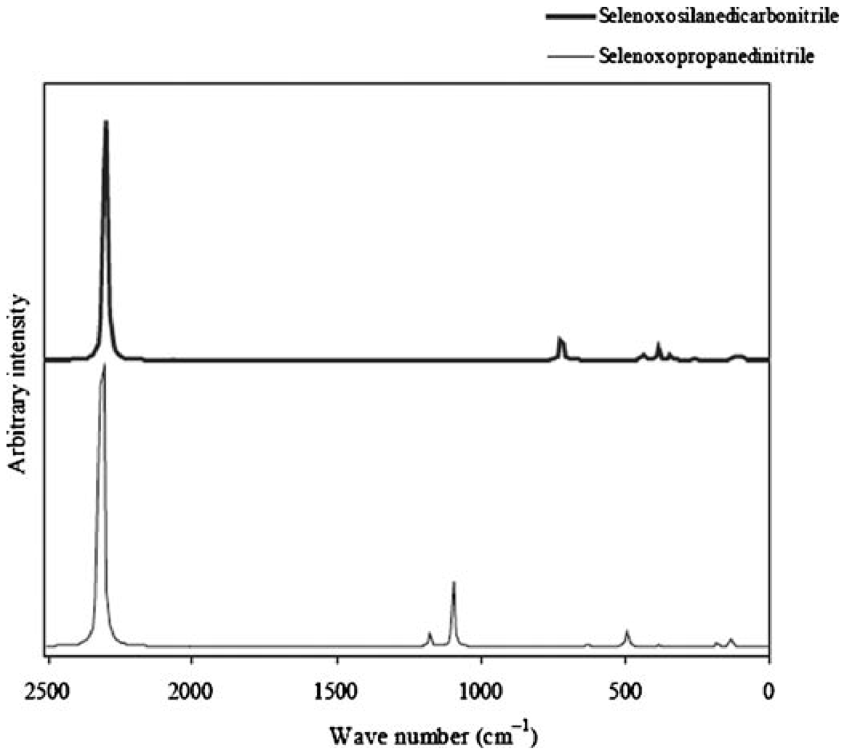


FIGURE 4 Simulated Raman spectra of selenoxopropanedinitrile and selenoxosilanedicarbonitrile.

The fundamental frequencies of an anharmonic oscillator may be written as

$$\nu_i = \nu_{0i} + 2X_{ii} + \frac{1}{2}\sum_{j \neq i} X_{ij} \qquad (3)$$

The rotational vibrational couplings [24,25] are determined in terms of the rotational, centrifugal, distortion, and rotational–vibrational constants and Coriolis coupling parameters [26].

RESULTS AND DISCUSSION

The gas-phase optimized structural parameters, energies, atomization energies, and HOMO–LUMO gaps of selenoxopropanedinitrile and selenoxosilanedicarbonitrile are presented in Table 1 and Fig. 2. To test these parameters obtained using B3LYP/cc-pVTZ calculations, MP2/cc-pVTZ calculations were also carried out to check the quality of the results. This is more important because to the best of out knowledge, these parameters are not

TABLE 4 Vibrational Parameters of Overtones of Selenoxopropanedinitrile and Selenoxosilanedicarbonitrile

Selenoxopropanedinitrile		*Selenoxosilanedicarbonitrile*		
Harmonic	*Anharmonic*	*Harmonic*	*Anharmonic*	*Assignment*
4630.0	4526.8	4590.7	4526.0	$2\nu_1$
2180.5	2140.2	1430.8	1424.0	$2\nu_2$
1239.0	1218.2	869.3	851.6	$2\nu_3$
984.3	977.5	763.0	755.3	$2\nu_4$
264.2	266.0	187.5	187.3	$2\nu_5$
762.8	760.1	513.6	511.1	$2\nu_6$
1266.7	1256.4	677.0	665.8	$2\nu_7$
415.5	412.8	256.4	255.8	$2\nu_8$
4604.5	4572.7	4586.1	4521.3	$2\nu_9$
2344.0	2319.5	1326.2	1315.5	$2\nu_{10}$
936.6	928.7	639.3	633.4	$2\nu_{11}$
355.7	355.0	231.2	229.5	$2\nu_{12}$

TABLE 5 Vibrational Parameters of Combination Tones of Selenoxopropanedinitrile and Selenoxosilanedicarbonitrile

Selenoxopropanedinitrile		*Selenoxosilanedicarbonitrile*		
Harmonic	*Anharmonic*	*Harmonic*	*Anharmonic*	*Assignment*
3405.3	3340.73	3010.7	2981.4	$\nu_2 + \nu_1$
2934.5	2877.6	2730.0	2694.2	$\nu_3 + \nu_1$
1709.8	1678.4	1150.1	1139.0	$\nu_3 + \nu_2$
2807.2	2758.6	2676.8	2645.4	$\nu_4 + \nu_1$
1582.4	1562.2	1096.9	1085.4	$\nu_4 + \nu_2$
1111.6	1105.8	816.2	805.2	$\nu_4 + \nu_3$
2447.2	2401.1	2389.1	2361.7	$\nu_5 + \nu_1$
1222.4	1205.8	809.2	807.3	$\nu_5 + \nu_2$
751.6	742.9	528.4	520.1	$\nu_5 + \nu_3$
624.3	623.8	475.2	471.3	$\nu_5 + \nu_4$
2696.4	2645.0	2552.1	2521.0	$\nu_6 + \nu_1$
1471.7	1452.3	972.2	969.1	$\nu_6 + \nu_2$
1000.9	985.0	691.5	674.8	$\nu_6 + \nu_3$
873.5	868.5	638.3	631.0	$\nu_6 + \nu_4$
513.5	512.1	350.5	347.6	$\nu_6 + \nu_5$
2948.4	2894.0	2633.8	2601.7	$\nu_7 + \nu_1$
1723.6	1695.2	1053.9	1055.8	$\nu_7 + \nu_2$
1252.8	1237.2	773.2	760.7	$\nu_7 + \nu_3$
1125.5	1116.9	720.0	711.5	$\nu_7 + \nu_4$
765.4	760.0	432.2	427.9	$\nu_7 + \nu_5$
1014.7	1002.9	595.3	579.8	$\nu_7 + \nu_6$
2522.8	2475.3	2423.5	2396.2	$\nu_8 + \nu_1$
1298.0	1279.6	843.6	841.0	$\nu_8 + \nu_2$
827.2	818.8	562.9	555.2	$\nu_8 + \nu_3$
699.9	702.0	509.7	506.4	$\nu_8 + \nu_4$
339.8	340.9	221.9	222.1	$\nu_8 + \nu_5$
589.1	586.9	385.0	382.3	$\nu_8 + \nu_6$
841.1	834.1	466.7	462.7	$\nu_8 + \nu_7$
4617.3	4538.1	4588.4	4512.5	$\nu_9 + \nu_1$
3392.5	3384.9	3008.4	2979.1	$\nu_9 + \nu_2$
2921.7	2900.4	2727.7	2691.7	$\nu_9 + \nu_3$
2794.4	2781.8	2674.5	2643.0	$\nu_9 + \nu_4$
2434.3	2424.1	2386.8	2359.3	$\nu_9 + \nu_5$
2683.6	2668.1	2549.8	2518.6	$\nu_9 + \nu_6$
2935.5	2916.8	2631.5	2599.3	$\nu_9 + \nu_7$
2510.0	2498.3	2421.2	2393.9	$\nu_9 + \nu_8$
3487.0	3396.9	2958.5	2927.8	$\nu_{10} + \nu_1$
2262.2	2207.0	1378.5	1370.8	$\nu_{10} + \nu_2$
1791.4	1770.3	1097.8	1081.0	$\nu_{10} + \nu_3$
1664.1	1648.0	1044.6	1034.3	$\nu_{10} + \nu_4$
1304.1	1291.2	756.9	753.6	$\nu_{10} + \nu_5$
1553.4	1539.4	919.9	922.7	$\nu_{10} + \nu_6$
1805.3	1786.1	1001.6	1002.5	$\nu_{10} + \nu_7$
1379.7	1365.6	791.3	788.1	$\nu_{10} + \nu_8$
3474.2	3470.6	2956.2	2925.5	$\nu_{10} + \nu_9$
2783.3	2731.1	2615.0	2584.3	$\nu_{11} + \nu_1$
1558.6	1537.3	1035.1	1033.4	$\nu_{11} + \nu_2$
1087.8	1067.9	754.3	746.6	$\nu_{11} + \nu_3$
960.5	953.2	701.2	695.7	$\nu_{11} + \nu_4$
600.4	597.6	413.4	410.7	$\nu_{11} + \nu_5$
849.7	843.4	576.5	571.9	$\nu_{11} + \nu_6$
1101.7	1092.2	658.2	652.4	$\nu_{11} + \nu_7$
676.1	671.9	447.9	445.7	$\nu_{11} + \nu_8$
2770.6	2754.2	2612.7	2582.0	$\nu_{11} + \nu_9$
1640.3	1628.6	982.8	970.9	$\nu_{11} + \nu_{10}$
2492.9	2445.7	2410.2	2383.0	$\nu_{12} + \nu_1$
1268.1	1249.6	831.0	827.6	$\nu_{12} + \nu_2$
797.3	786.7	550.3	541.4	$\nu_{12} + \nu_3$

(Continued)

TABLE 5 (Continued)

Selenoxopropanedinitrile		*Selenoxosilanedicarbonitrile*		
Harmonic	*Anharmonic*	*Harmonic*	*Anharmonic*	*Assignment*
670.0	667.2	497.1	491.4	$\nu_{12} + \nu_4$
309.9	310.8	209.3	208.6	$\nu_{12} + \nu_5$
559.2	556.5	372.4	368.6	$\nu_{12} + \nu_6$
811.2	804.6	454.1	449.1	$\nu_{12} + \nu_7$
385.6	385.3	243.8	243.2	$\nu_{12} + \nu_8$
2480.1	2468.7	2408.6	2380.7	$\nu_{12} + \nu_9$
1349.8	1335.9	778.7	774.9	$\nu_{12} + \nu_{10}$
646.2	643.0	435.3	434.1	$\nu_{12} + \nu_{11}$

available experimentally for comparison. The results from Table 1 allow some conclusions to be drawn. First, there is a good agreement for the parameters obtained using the two methods of calculations. Second, the C≡N bond length is predicted to be longer by the MP2 method, but the bond length is not much affected when carbon is being substituted by silicon. Third, for both compounds, the bond angles ∠CCC and ∠CSiC are predicted to be nearly the same by the two methods. However, the bond angle ∠CCC is larger than the bond angle ∠CSiC, and this may be due to more repulsion between the carbon atoms in selenoxopropanedinitrile. Finally, two parameters, namely, μ and η, calculated using HOMO and LUMO energies, are also included in Table 1. In DFT framework [27], μ and η are calculated as

$$\mu \cong \frac{1}{2}(E_{\text{LUMO}} + E_{\text{HOMO}}) \qquad (4)$$

$$\eta \cong \frac{1}{2}(E_{\text{LUMO}} - E_{\text{HOMO}}) \qquad (5)$$

The significances of μ and η are that μ is related to charge transfer processes and η is related to chemical hardness. In this case, the values of μ indicate that charge transfer processes are more predominant in selenoxopropanedinitrile and this may favor stabilization through hyperconjugative interactions. The values of η indicate that selenoxopropanedinitrile is harder than selenoxosilanedicarbonitrile.

TABLE 6 Rotational and Wilson Centrifugal Distortion Constants (in MHz) of Selenoxopropanedinitrile and Selenoxosilanedicarbonitrile

	Selenoxopropanedinitrile	*Selenoxosilanedicarbonitrile*
A_e	2971.3	2375.3
B_e	1902.3	1234.5
C_e	1159.8	812.3
A_o	0.000912	0.000412
B_o	−0.0022805	−0.001202
C_o	0.0027576	0.002782

Natural charges of the atoms of selenoxopropanedinitrile and selenoxosilanedicarbonitrile, calculated using NBO analysis [28], are presented in Table 2. These charges may be interpreted using the electronegativity of the atoms [29].

The title compounds are planar molecules having the C_{2v} point group of symmetry. Their 12 modes of vibrations account for the irreducible representations $\Gamma_v = 5A_1 + A_2 + 2B_1 + 4B_2$ of the C_{2v} point group. The calculated vibrational infrared frequencies and intensities, with appropriate assignments, are reported for the fundamental modes, the first overtones, and the combination tones in the harmonic and anharmonic approximations in Tables 3–5. Raman frequencies and intensities are also included in Table 3. The simulated infrared and Raman spectra are illustrated in Figs. 3 and 4, respectively. The spectra in Fig. 3 are mostly dominated by the stretching frequencies of C≡N, C═Se, and Si≡Se bonds. The spectra in Fig. 4 show that stretching of C≡N is the one with highest Raman activity. The data from Table 3 indicate that when carbon in selenoxopropanedinitrile is substituted by silicon, it is only those vibrations involving the C═Se that are mainly affected. In addition, the combination tone $\nu_5 + \nu_4$ may be in Fermi resonance with ν_3 and the combination tone $\nu_{12} + \nu_8$ may be in Fermi resonance with ν_6 for selenoxopropanedinitrile. Furthermore, the combination tone $\nu_{12} + \nu_{11}$ may be in Fermi resonance with ν_3 for selenoxosilanedicarbonitrile.

The calculated rotational and Wilson centrifugal distortion constants are summarized in Table 6. Anharmonic vibrations result in the coupling between the normal modes and these lead to shift in the vibrational frequencies. The anharmonicity constants from Eq. (2) are given in Tables 7 and 8. These constants may be used to explain that, in general, fundamental frequencies, overtones, and

TABLE 7 Calculated Anharmonicity Constants of Selenoxopropanedinitrile

X_{ij}	1	2	3	4	5	6	7	8	9	10	11	12
1	−5.721	–	–	–	–	–	–	–	–	–	–	–
2	−1.636	−3.178	–	–	–	–	–	–	–	–	–	–
3	−1.767	−5.127	−1.183	–	–	–	–	–	–	–	–	–
4	−0.828	−1.340	5.174	−1.550	–	–	–	–	–	–	–	–
5	−0.805	−0.254	−0.106	0.381	0.243	–	–	–	–	–	–	–
6	−2.928	0.270	−4.051	−0.625	0.567	1.222	–	–	–	–	–	–
7	−2.411	−5.364	−0.448	−0.803	−0.074	−3.252	0.852	–	–	–	–	–
8	−1.184	−0.975	1.151	4.344	0.811	0.682	−0.588	−0.949	–	–	–	–
9	−23.122	19.576	−2.009	−0.634	−0.774	−2.837	−2.698	−1.131	−5.780	–	–	–
10	−31.030	−25.040	1.260	−1.055	−0.369	1.773	−0.017	−0.518	19.690	0.955	–	–
11	−2.515	−0.449	−6.904	−1.625	0.287	0.037	0.382	0.032	−2.478	5.318	−0.197	–
12	−0.721	−0.964	−0.881	−0.461	0.697	0.322	−0.124	−0.422	−0.748	−0.237	1.102	0.155

TABLE 8 Calculated Anharmonicity Constants of Selenoxosilanedicarbonitrile

X_{ij}	1	2	3	4	5	6	7	8	9	10	11	12
1	−5.564	–	–	–	–	–	–	–	–	–	–	–
2	−0.551	−1.379	–	–	–	–	–	–	–	–	–	–
3	−1.113	−1.065	−0.916	–	–	–	–	–	–	–	–	–
4	−0.653	−5.440	1.056	0.187	–	–	–	–	–	–	–	–
5	−0.460	−0.372	−0.257	0.230	0.067	–	–	–	–	–	–	–
6	−1.853	1.476	−6.199	−0.720	0.289	1.289	–	–	–	–	–	–
7	−1.704	7.614	−0.842	−0.740	−0.483	−9.256	−1.925	–	–	–	–	–
8	−0.444	−0.459	0.310	0.791	0.365	−0.123	−0.209	−0.228	–	–	–	–
9	−22.227	−0.534	−1.210	−0.642	−0.449	−1.855	−1.748	−0.420	−5.568	–	–	–
10	−0.414	−2.169	−0.537	−0.283	0.345	8.765	7.973	0.329	−0.410	−1.889	–	–
11	−1.582	2.733	2.531	0.963	−0.220	0.270	0.219	0.293	−1.580	−6.083	−0.643	–
12	−0.324	−0.514	−0.055	−0.837	0.258	−0.416	−0.461	−0.313	−0.316	0.486	0.345	−0.031

combination tones are generally lower under anharmonic approximation than under harmonic approximation. In those cases in which the last statement is not valid, deviations are due to interactions between vibrational modes and Fermi resonance. The calculated values of rotational–vibration coupling constants are reported in Table 9. Jahn's rule [30] has been used to work out the Coriolis coupling coefficients $\zeta\ (I, J)$ between the various vibrational modes. The constants in Tables 6–10 should be useful in the interpretation of future experimental investigations.

TABLE 9 Rotation–Vibration Coupling Constants (in MHz) of Selenoxopropanedinitrile and Selenoxosilanedicarbonitrile

	Selenoxopropanedinitrile			*Selenoxosilanedicarbonitrile*		
	a	*b*	*c*	*a*	*b*	*c*
α_1	8.2	2.2	2.1	5.8	1.0	1.1
α_2	16.2	−0.5	4.1	8.4	0.8	0.7
α_3	11.2	−1.9	−0.8	13.1	−5.5	−0.5
α_4	−8.7	7.2	1.6	−8.6	2.9	0.7
α_5	−8.2	−2.7	0.8	−7.9	−1.0	0.6
α_6	−8.0	5.4	−1.1	−7.4	2.3	−1.1
α_7	0.02	−7.1	−1.0	−12.0	0.5	−0.8
α_8	−10.9	−2.7	−2.1	−18.8	−2.1	−1.3
α_9	8.0	2.8	2.2	6.1	0.9	1.1
α_{10}	−2.5	10.6	2.3	−2.5	4.5	2.6
α_{11}	−8.5	−1.2	−0.1	1.5	−1.4	−0.5
α_{12}	1.2	−2.8	−1.9	11.4	−2.1	−1.5

TABLE 10 Coriolis Coupling Between Different Vibrational Modes for Carbonyl Cyanide of Selenoxopropanedinitrile and Selenoxosilanedicarbonitrile[a]

Vibration	*Modes*		*X-components: Coriolis Coupling ζ (I, J)*	*Modes*		*Y-components: Coriolis Coupling ζ (I, J)*	*Modes*		*Z-components: Coriolis Coupling ζ (I, J)*
	I	*J*		*I*	*J*		*I*	*J*	
Selenoxopropanedinitrile									
1	9	1	0.0041	7	1	0.3563	6	1	0.8413
2	9	2	−0.2817	7	2	−0.8202	6	2	0.0812
3	9	3	−0.6915	7	3	−0.3957	6	3	0.4880
4	9	4	−0.4890	7	4	−0.2073	6	4	0.1752
5	9	5	−0.4510	7	5	−0.0289	6	5	0.1297
6	10	1	−0.1278	8	1	−0.3691	9	7	0.6205
7	10	2	0.8288	8	2	−0.5058	9	8	−0.5894
8	10	3	0.0975	8	3	0.4321	10	7	−0.7201
9	10	4	−0.1389	8	4	0.4817	10	8	−0.6220
10	10	5	−0.5177	8	5	0.4349	11	7	−0.3092
11	11	1	−0.8860	9	6	0.5010	11	8	0.3045
12	11	2	0.1143	10	6	0.0841	12	7	−0.0289
13	11	3	−0.2957	11	6	0.8307	12	8	−0.4160
14	11	4	0.0344	12	6	−0.2278			
15	11	5	0.3368						
16	12	1	0.4243						
17	12	2	0.4597						
18	12	3	−0.4211						
19	12	4	−0.2323						
20	12	5	0.6143						
Selenoxosilanedicarbonitrile									
1	9	1	0.0013	7	1	−0.4713	6	1	0.8013
2	9	2	−0.1665	7	2	−0.6415	6	2	−0.3785
3	9	3	0.6471	7	3	0.4657	6	3	0.5007
4	9	4	−0.5899	7	4	−0.3805	6	4	−0.2890
5	9	5	−0.4534	7	5	−0.0686	6	5	−0.1492
6	10	1	0.0624	8	1	0.3313	9	7	0.6631
7	10	2	0.6911	8	2	−0.6902	9	8	−0.4671
8	10	3	−0.2812	8	3	−0.2102	10	7	−0.5605
9	10	4	0.0060	8	4	0.4160	10	8	−0.6886
10	10	5	−0.6629	8	5	0.4434	11	7	0.4950
11	11	1	−0.9094	9	6	−0.5695	11	8	−0.1891
12	11	2	−0.2467	10	6	0.0198	12	7	0.0333
13	11	3	−0.2260	11	6	0.7985	12	8	0.5215
14	11	4	0.0094	12	6	−0.1945			
15	11	5	−0.2469						
16	12	1	0.3892						
17	12	2	−0.6497						
18	12	3	−0.2768						
19	12	4	0.2807						
20	12	5	−0.5206						

[a] Vibration modes are per Tables 3–5.

CONCLUDING REMARKS

In summary, this paper has presented the optimized geometrical parameters and vibrational spectroscopic parameters of two novel compounds, namely, selenoxopropanedinitrile and selenoxosilanedicarbonitrile, using B3LYP/cc-pVTZ calculations in the gas phase. The results of this study are reported for the first time and should be useful for the characterization of the title compounds as and when they are synthesized. The results of our research show that silicon for carbon substitution affects mainly those properties that are dependent on the C=Se bond.

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