

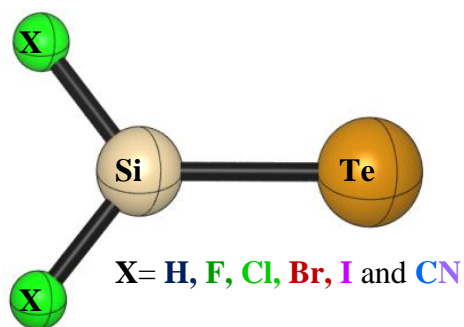
Structures, Energetics and Reactivities of Novel Silanetellurones: A Computational Study

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Di-substituted silanetellurones, $X_2Si=Te$ ($X=H, F, Cl, Br, I$ and CN) are the target of this research. They are organometallic analogues, also known as heavy ketones, and they have recently been of great interest to researchers. Knowledge of the properties of such heavy ketones is important for a better understanding of both the chalcogen and substituent effects. The chemistry of multi-bonded compounds between group 14 and heavier chalcogen atoms has attracted chemists in various fields, as these molecules have proven to be convenient models for studying fundamental chemical problems and valuable intermediate products in synthesis. However, the literature of the mentioned species is limited and this research work endeavors a systematic investigation of these silanetellurones, using theoretical methods. We report the structural and spectroscopic parameters as well as the ionization potentials (IP_{ad} and $IP_{ad(ZPVE)}$), the neutral–anion separations (EA_{ad} and $EA_{ad(ZPVE)}$), the singlet–triplet splittings, the Kohn–Sham HOMO–LUMO gaps besides the nucleophilicity (N) and global electrophilicity (ω) indices. Since experimental data are still lacking for silanetellurones, the findings of this work would add to the literature, assist experimentalists to generate and further explore these novel species as well as rationalize some reactions pertaining to silanetellurones.

1.0 Introduction

The 20th century saw an explosion in the number and range of commercial applications of materials derived from the element silicon [1]. Since then organosilicon chemistry has been an important field of research. Recent exciting advances made in the use of new concepts to rationalize the synthetic chemistry of organosilicon compounds and their applications [2,3] are catalyzing further studies involving such compounds. The use of organosilicon reagents for organic synthesis and as intermediates is now becoming a field of great importance [4].

Studies on the $XYC=Z$ ($X, Y=H, F, Cl, Br$ and I ; $Z=O, S, Se$ and Te) are well under way. Substituting the oxygen atom in formaldehyde by sulfur, selenium or tellurium increases the chalcogen character of the molecule, which in turn decreases the stability of the $C=Z$ bond but increases the shift in the ionization potential significantly. Moreover, lowering of the energy level of the π^* orbital facilitates addition of an extra electron, which in turn make the electron affinities become more positive down $H_2C=Z$ ($Z=O, S, Se$ and Te) carbonyl series [5].

Our previous work [6] shed light on the theoretical prediction of the structural parameters and energetics of telluroformaldehyde and its derivatives as novel organometallics. Silanones ($X_2Si=O$) [7-15], silanethiones ($X_2Si=S$) [16-20] and silaneselenones ($X_2Si=Se$) [21,22] have been subjected to various studies in the past years, however, silanetellurones ($X_2Si=Te$) have not yet been explored. The aim of this research is to investigate theoretically, molecular geometries, spectroscopic parameters and energetics of some di-substituted silanetellurones, over and above to help in rationalizing some reactions pertaining to these heavy ketones.

2.0 Methodology

Density functional theory (DFT) and second order Møller-Plesset perturbation theory (MP2) [23] computations were performed using the Gaussian 03 program [24] to fully optimize the species independently in the gas phase. The functionals used at the DFT level are B3LYP, BLYP and BHLYP [25-27].

The basis sets used for all atoms (except iodine and tellurium) in this work are of double- ζ plus polarization quality with additional s- and p-type diffuse functions, and denoted DZP++. The LANL2DZdp ECP [28-30] and 6-311G(*d,p*) [31] basis sets are used for tellurium and iodine atoms.

Zero-point vibrational energies (ZPVE) are evaluated at each level. The corrected ionization potential $IP_{ad(ZPVE)}$ and the corrected adiabatic electron affinities $EA_{ad(ZPVE)}$ are reported as follows:

$$IP_{ad(ZPVE)} = E(\text{optimized cation} + ZPVE_{\text{cation}}) - E(\text{optimized neutral} + ZPVE_{\text{neutral}})$$
$$EA_{ad(ZPVE)} = E(\text{optimized neutral} + ZPVE_{\text{neutral}}) - E(\text{optimized anion} + ZPVE_{\text{anion}})$$

Each singlet–triplet splitting is predicted as the energy difference between the neutral ground state and the lowest–lying triplet state.

The nucleophilicity index, N , which was introduced by Domingo *et al.* [32], is calculated using the equation, $N = E_{HOMO(Nu)} - E_{HOMO(TCNE)}$, where tetracyanoethylene (TCNE) is chosen as the reference.

The global electrophilicity, ω , [33] is also calculated following the expression, $\omega = (\mu^2/2\eta)$, where μ is the chemical potential given by, $\mu \approx (E_{HOMO} + E_{LUMO})/2$ and η is the chemical hardness, $\eta = (E_{LUMO} - E_{HOMO})$ [34,35].

3.0 Results and Discussion

3.1 Molecular Geometries

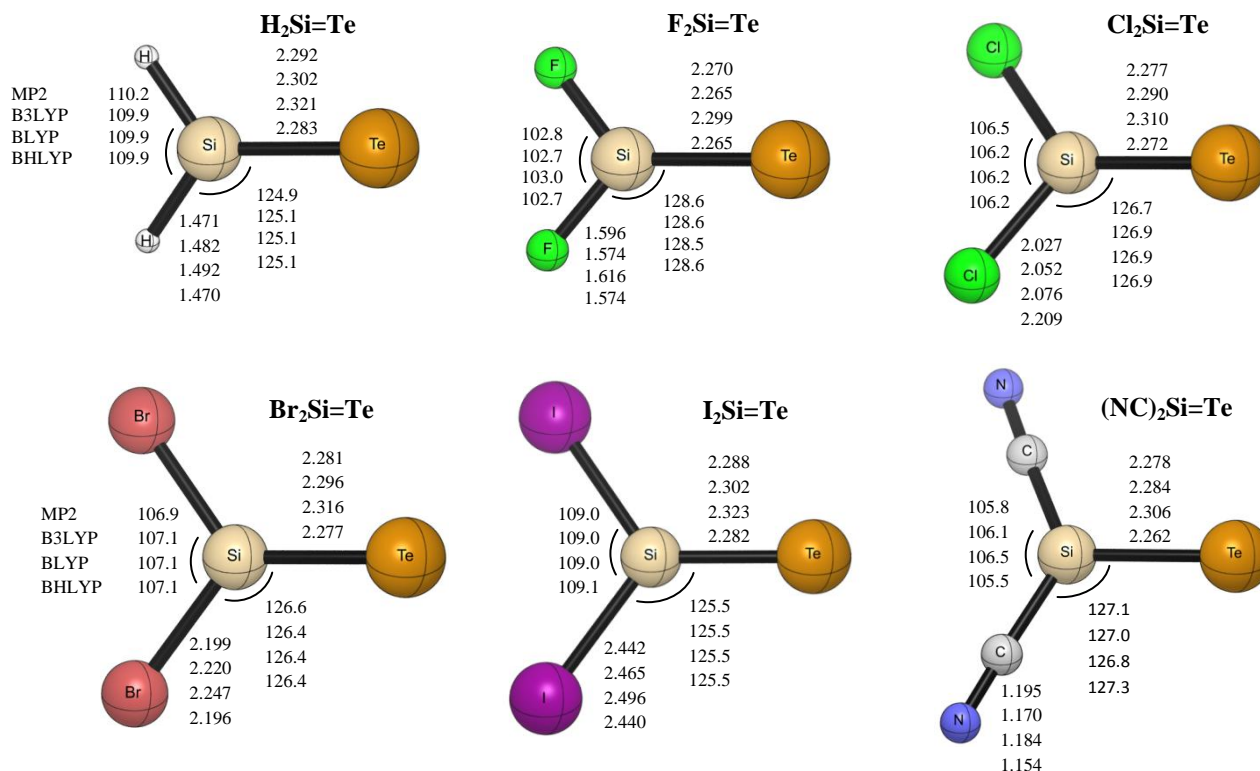


Figure 1: Equilibrium geometries (bond lengths in Å, bond angles in °) for the neutral ground state (¹A', C_{2v}) of all the scrutinized silanetellurones.

The Si=Te and Si-X bond distances elongate in the order H < F < CN < Cl < Br < I. These expected trends are due to the change in atomic sizes and electronegativities (χ) of the substituents, except for the H derivatives.

The shortening of the Si=Te bond upon increasing electronegativity of substituent X, can be explained in terms of the inherent polarity of the Si=Te bond. Si ($\chi = 1.90$) is more electropositive than Te ($\chi = 2.10$) and therefore the Si=Te bond is expected to be highly polarized in the sense Si^{δ+}=Te^{δ-}.

The more electronegative the substituent bonded to silicon, the more positive charge at silicon, the higher the degree of bond ionicity, and the shorter the Si=Te double bond becomes.

Figures 2-4 summarizes the structural changes observed for the di-substituted silanetellurones compared to the literature of analogous formaldehyde, silanone and telluroformaldehyde derivatives.

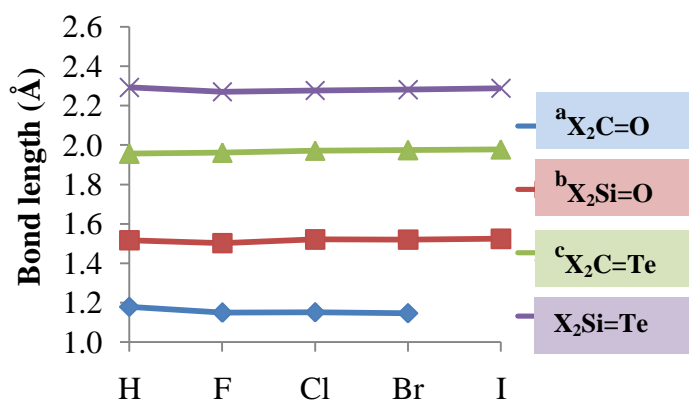
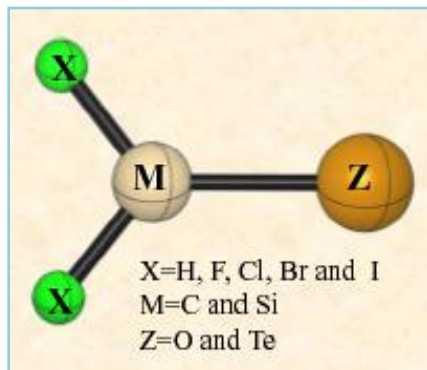


Figure 2: Trends in M=Z Bond Lengths

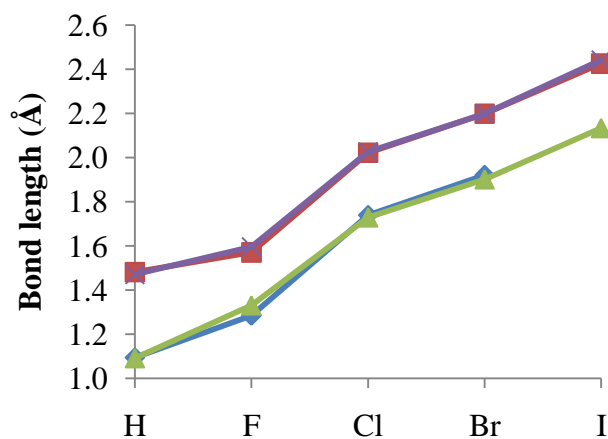


Figure 3: Trends in M-X Bond Lengths

a=ref 36, b=ref 7, c=ref 6

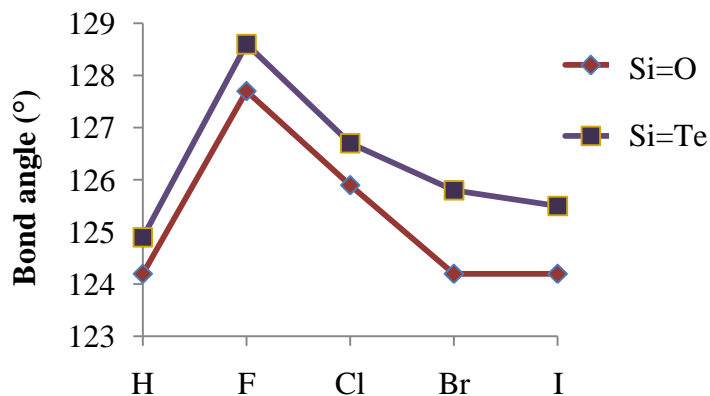
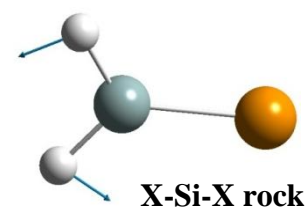
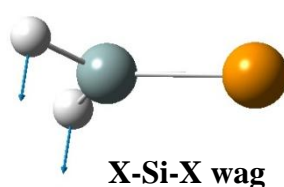
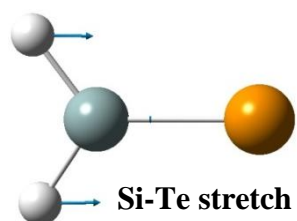


Figure 4: Trends in X-M-Z Bond Angle

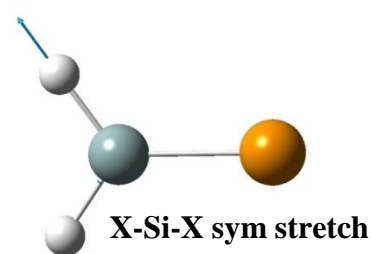
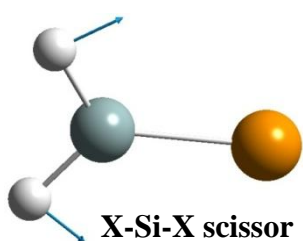
3.2 Harmonic Vibrational Frequencies

The 6 modes of vibrations of silanetellurone account for the irreducible representations, $\Gamma_v = 3A_1 + B_1 + 2B_2$ of the C_{2v} point group. Table 1 summarizes the unscaled infrared vibrational wavenumbers calculated in the harmonic approximation, their intensities and the assignment for each vibration for all the scrutinized silanetellurones.

Table 1: Vibrational wavenumbers (cm^{-1}) and IR intensities (km mol^{-1}) (in parentheses) of the $\text{X}_2\text{Si}=\text{Te}$ ($\text{X}=\text{H, F, Cl, Br, I}$ and CN) molecules.



$\text{H}_2\text{Si}=\text{Te}$	$\nu = 475.70$ (2.85)	$\nu = 576.14$ (6.14)	$\nu = 581.03$ (7.59)
$\text{F}_2\text{Si}=\text{Te}$	$\nu = 447.87$ (24.07)	$\nu = 247.79$ (12.63)	$\nu = 189.55$ (2.31)
$\text{Cl}_2\text{Si}=\text{Te}$	$\nu = 654.10$ (227.61)	$\nu = 196.58$ (2.52)	$\nu = 141.34$ (0.76)
$\text{Br}_2\text{Si}=\text{Te}$	$\nu = 584.5$ (153.63)	$\nu = 171.60$ (0.80)	$\nu = 100.01$ (0.24)
$\text{I}_2\text{Si}=\text{Te}$	$\nu = 545.02$ (107.40)	$\nu = 154.18$ (0.04)	$\nu = 81.78$ (0.12)
$(\text{NC})_2\text{Si}=\text{Te}$	$\nu = 690.80$ (98.30)	$\nu = 312.12$ (0.01)	$\nu = 295.81$ (0.01)



$\text{H}_2\text{Si}=\text{Te}$	$\nu = 1041.62$ (188.93)	$\nu = 2324.87$ (102.13)	$\nu = 2336.58$ (98.17)
$\text{F}_2\text{Si}=\text{Te}$	$\nu = 275.40$ (16.13)	$\nu = 919.67$ (325.42)	$\nu = 937.77$ (157.47)
$\text{Cl}_2\text{Si}=\text{Te}$	$\nu = 176.30$ (5.96)	$\nu = 337.28$ (0.73)	$\nu = 612.80$ (163.24)
$\text{Br}_2\text{Si}=\text{Te}$	$\nu = 113.5$ (1.63)	$\nu = 232.67$ (4.82)	$\nu = 480.78$ (135.20)
$\text{I}_2\text{Si}=\text{Te}$	$\nu = 84.33$ (0.43)	$\nu = 181.04$ (4.29)	$\nu = 411.31$ (127.50)
$(\text{NC})_2\text{Si}=\text{Te}$	$\nu = 421.01$ (3.35)	$\nu = 2062.68$ (101.06)	$\nu = 2064.09$ (47.30)

3.3 Ionization Potential

The correlation between the substituent X and/or Y with the energy differences between the neutral and the corresponding cationic species is presented in Figure 5.

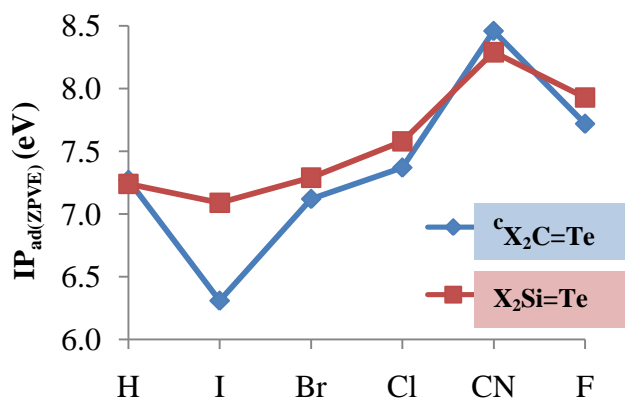


Figure 5: Ionization Potential as a Function of the Substituents

The ionization potential of the molecules upon substituent replacement falls in the order $CN > F > Cl > Br > I$, in agreement with the electronegativities of the substituents, except the cyano derivatives.

The presence of a strongly electron withdrawing atom or a strong π acceptor substituent, being directly attached to the silicon atom:

- reduces the population of the 3s and 3p orbitals of silicon,
- increases the backbonding from Te

Hence the polarity of the Si=Te bond increases, and it becomes more difficult to remove an electron from the molecular orbital of the silanetellurones.

3.4 Electron Affinity

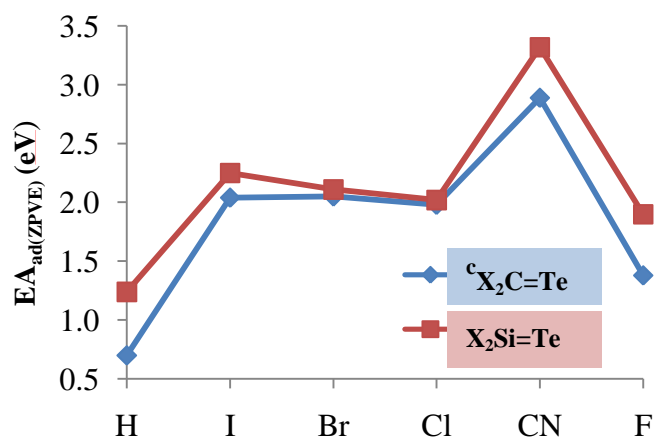


Figure 6: Electron Affinity as a Function of the Substituents

Upon increasing electronegativity, an abrupt decrease in electron affinity could conceivably be expected.

However, the *contrary* is observed as:

the more electronegative the substituent the more +ve the charge at the Si atom and the better the π donation from the chalcogen and the heteroatom lone pairs.

3.5 Singlet-triplet Splittings

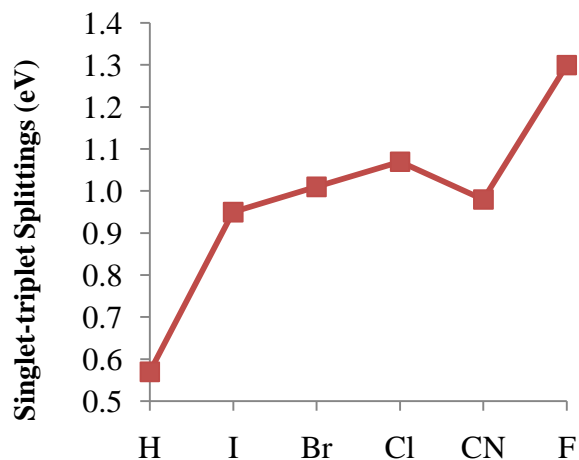


Figure 7: ΔE_{S-T} of $X_2Si=Te$ species as a function of the substituents

The Silanetellurones have 2 valence electrons, for instance the electronic configuration of $H_2Si=Te$ is $(1a_1)^2$, $(2a_1)^2$, $(3b_1)^2$, $(4a_1)^2$, $(5b_2)^2$, $(6a_1)^2$, $(7a_1)^2$, $(8b_2)^2$, $(9a_1)^2$, $(10b_1)^2$, $(11b_2)^2$.

Therefore both the singlet and triplet species may arise.

The electron-attracting substitutions on the double bond enlarge the ΔE_{S-T} value of the silanetellurones in favor of the singlet state.

Generally the low ΔE_{S-T} values predict that the silanetellurones can be classified as *soft molecules* having *high reactivities* and *low kinetic stabilities*.

3.6 Kohn-Sham HOMO-LUMO Gaps

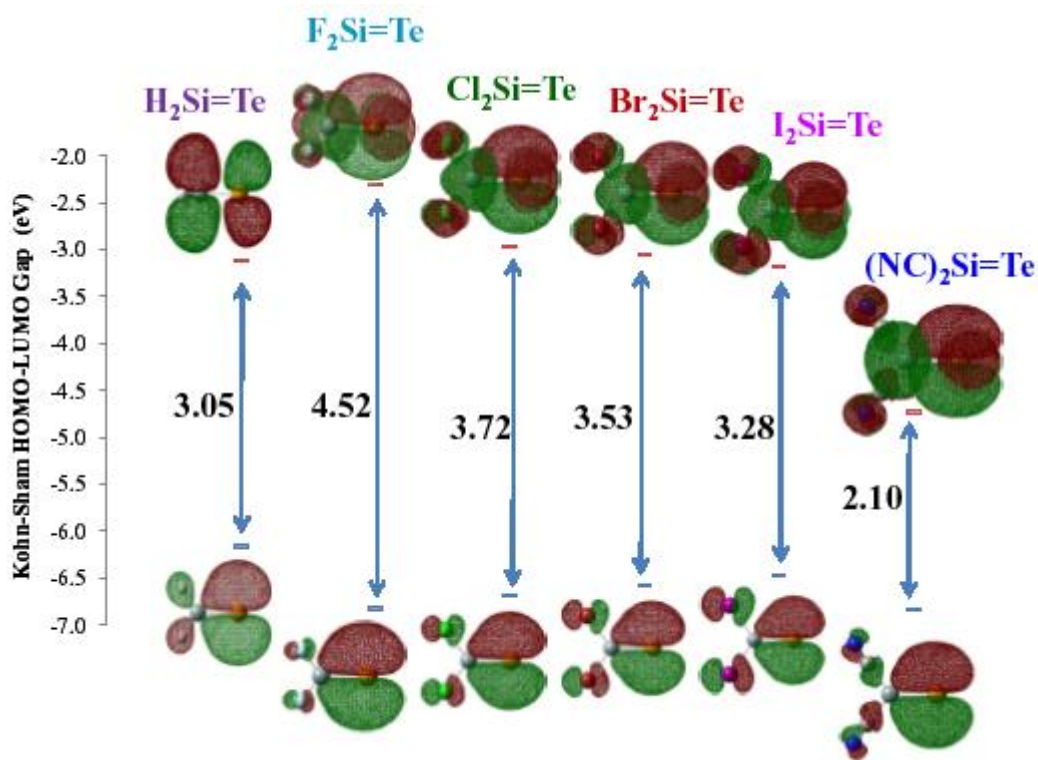


Figure 8: Frontier molecular orbitals and ΔE_{H-L} of all the scrutinized Silanetellurones.

- ✓ The HOMO of these heavy ketones is an n-orbital that corresponds to a lone pair on the chalcogen (Te) atom while the LUMO is a π^* orbital.
- ✓ HOMO distribution of the neutral species suggests that the Si=Te bond is conjugated, as it provides a clear path for electrons to flow.
- ✓ Since the energy level of the π^* orbital is lowered, the addition of an extra electron is facilitated, which in turn agrees with the positive electron affinities of the silanetellurones.
- ✓ HOMO–LUMO gaps are traditionally associated with chemical stability against electronic excitations, with larger gaps corresponding to greater kinetic stability.
- ✓ The ΔE_{H-L} values for silanetellurones fall in the range of 2.10-4.52 eV, comparable to those of telluroformaldehydes (1.98-3.42 eV) with $(NC)_2X=Te$ and $F_2X=Te$ ($X=C$ and Si), as the bookends in both cases. Thus silanetellurones should have similar stabilities as telluroformaldehydes [6].
- ✓ The HOMO and LUMO states are naturally attached to the concepts of nucleophilicity and electrophilicity, respectively. Table 2 reports the nucleophilicity (N) and global electrophilicity (ω) indices of all the scrutinized silanetellurones.

Table 2: Nucleophilicity (N) and Global Electrophilicity (ω) Indices for the Singlet Ground States of the $X_2Si=Te$ Molecules

	HOMO (eV)	LUMO (eV)	ΔE_{H-L} (eV)	N (eV)	ω (eV)
H₂Si=Te	-6.17	-3.11	3.05	3.25	3.53
F₂Si=Te	-6.82	-2.30	4.52	2.60	2.30
Cl₂Si=Te	-6.69	-2.96	3.72	2.73	3.13
Br₂Si=Te	-6.58	-3.05	3.54	2.84	3.28
I₂Si=Te	-6.47	-3.18	3.28	2.95	3.55
(NC)₂Si=Te	-6.83	-4.73	2.10	2.59	7.96

It is found that the stabilized LUMO states make the silanetellurones more electrophilic.

4.0 Conclusions

- The energetics of the di-substituted silanetellurones, $X_2Si=Te$, can be rationalized in terms of the electronegativity of the substituents, the electron density around the Si and Te atoms as well as the σ -donation and π backbonding of the substituents and the chalcogen.
- Good agreement between the results obtained for all the scrutinized $X_2Si=Te$ molecules and the literature telluroformaldehydes and silanones.
- The Kohn-Sham HOMO–LUMO separations of the molecules studied in this research work are small, within the range of 2.10–4.52 eV, suggesting the existence of a rich spectrum for $X_2Si=Te$ compounds in the visible regions.
- Based on the calculated nucleophilic and global electrophilic indices, the silanetellurones are reactive towards nucleophilic reagents. Therefore novel complexes of silanetellurones should be stable and easily synthesized.
- Since experimental data are still lacking, this work should add to the literature and assist experimental studies on organosilicon chemistry in the future.

Future works:

- ✓ Modelling of $XYSi=Te$, $X_2Ge=Te$ and $XYGe=Te$ (X, Y= H, F, Cl, Br, I and CN) compounds.
- ✓ Studying their kinetic and thermodynamic stabilities.
- ✓ Working out some reactions pertaining to these heavy ketones.

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