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DFT Insights into Substituent Effects on Trithiocarbonate Linkages: Electronic Structure, Stability, and Reactivity

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Abstract: This study provides a comprehensive theoretical investigation of trithiocarbonate (TTC) linkages, significant in polymerization processes, pharmacological therapies, and biologically active compounds. The focus is on the impact of various substituents on electronic structure, stability, and reactivity using Density Functional Theory (DFT). Key electronic parameters such as HOMO, LUMO, and energy gap were analyzed to evaluate molecular stability and potential reactivity. Compound characterization was performed using UV-visible absorption and IR spectroscopy. Molecular electrostatic potential (MEP) analysis identified nucleophilic and electrophilic regions, while the density of states (DOS) provided additional insights into electronic distribution. Global reactivity descriptors, including chemical potential (μ), chemical softness (s), chemical hardness (η), and electrophilicity index (ω), were used to assess the stability and reactivity. The electrophilic index of **TTC1–TTC11** ranged from 1.5 eV to 4.0 eV, indicating high reactivity, while **TTC12**, **TTC13**, and **TTC14** were classified as super-electrophilic. MEP analysis highlighted reactive sites, such as the sulfur atom in **TTC11** and the C-H bond in **TTC13**. High bond dissociation energies (BDE) and Gibbs free energies for **TTC11**, **TTC13**, and **TTC14** suggest strong linkages with their substituents when directly attached to ring-structured substituents without alkyl spacer. In contrast, **TTC8**, **TTC9**, **TTC10**, and **TTC12** exhibit weaker linkages when linked with alkyl spacer. These findings offer valuable insights for designing TTC compounds with tailored properties.

Keywords: Trithiocarbonate, Structural Reactivities, Molecular Electrostatic Potential, Chemical Reactivity Parameters, DFT

1. Introduction:

Trithiocarbonates (TTCs) are sulfur-rich compounds frequently widely used in controlled radical polymerization, pharmaceutical therapies, and biologically active compounds, owing to their unique stability and reactivity. Trithiocarbonates consist of a central carbon atom bonded to three sulfur

atoms, distinguishing them from dithiocarbonates by the presence of an additional sulfur atom in their structure. Substitutions on the trithiocarbonate core, typically represented by the general formula R_2CS_3 , where R is an organic group, can greatly influence its reactivity, electronic properties, and overall chemical behaviour. Because of their unique properties and reactivity, these compounds are of great interest in a variety of fields, including organic chemistry,¹ materials science,² polymer chemistry,³ coordination chemistry,⁴ nanotechnology,⁵ nanoparticle stabilization,⁵ surface modification,⁶ nanocarriers for gene delivery,⁷ biodegradable scaffolds,⁷ and targeted therapies.⁸ TTC derivatives have several commercial,⁹ synthetic, and medicinal uses.¹⁰ **Figure 1** illustrates substituted TTCs, which are utilized in a wide range of applications, including environmental solutions,¹¹ insecticides,¹² and agricultural pesticides.¹³ They also have roles as anticancer agents,¹⁴ antimicrobials,¹⁵ trithiocarbonate-organoclay nanohybrids interacting with MCF-7 cancer cells,¹⁶ radioprotective agent.¹⁷ Additionally, TTC derivatives function as histone deacetylase (HDAC) inhibitors,¹⁸ intrinsic photoredox catalysts,¹⁹ lubricating agents in oil additives,²⁰ as well as mineral removal from ores²¹, metal absorption,²² organic synthesis,²³ functionality preservation²⁴ and also employed in several C-C bond-building processes.²⁵ In addition, trithioaddition-fragmentation carbonate derivatives are generally used as reversible addition-fragmentation chain-transfer (RAFT) agents in free-radical polymerization processes,²⁶ vinylene trithiocarbonate (VTC) as the electrolyte additive for the lithium-ion,²⁷ organic trithiocarbonates,

like dibenzyl trithiocarbonates (DBTTC), can be applied to well-defined polymers or block copolymers with styrene, alkyl acrylate, acrylic acid, alkyl acrylamide, or acrylonitrile.²⁸

Our research group has been engaged from the past several years in the design and synthesis of biologically potent organosulfur compounds.²⁹⁻³¹ The primary objective of this study is to investigate how the TTC linkage affects the structural reactivities of various substituted TTCs. To achieve this, Density Functional Theory (DFT) calculations were employed to calculate the global chemical reactivity descriptors (such as HOMO, LUMO, energy gap, global hardness, and electrophilicity), which offer profound insights into the reactivity of trithiocarbonates. Understanding these parameters enables the optimization of TTCs for applications in controlled radical polymerization, material design, and organic synthesis, highlighting their role as efficient mediators in electron transfer and radical processes. Prior studies³²⁻³⁵ have suggested that the substitution pattern greatly influences the TTC's role as a mediator in radical reactions. This research aimed to explore the impact of various substituents, including alkyl, allyl, iso-butyl, sec-butyl, cyclohexyl, benzyl, phenethyl, p-tolyl, chlorobenzyl, thiophenyl, nitrophenyl, etc. on the TTC linkage, as illustrated in **Fig. 2**, using density functional theory (DFT) calculations. A comprehensive understanding of molecular characterization substituted TTCs was attained by combining DFT calculations with experimental findings. Notably, this study represents the first systematic evaluation of TTCs, exploring the influence of substituent groups (R)

through DFT calculations - as no previous reports have comprehensively addressed this aspect.

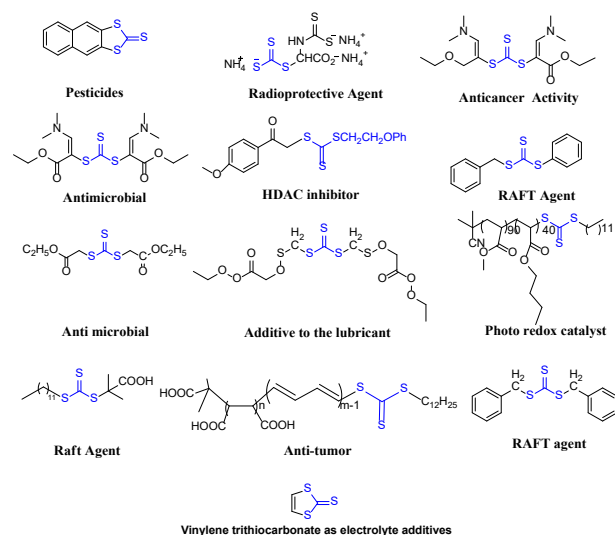


Figure 1: Structurally diverse biologically potent trithiocarbonate derivatives.

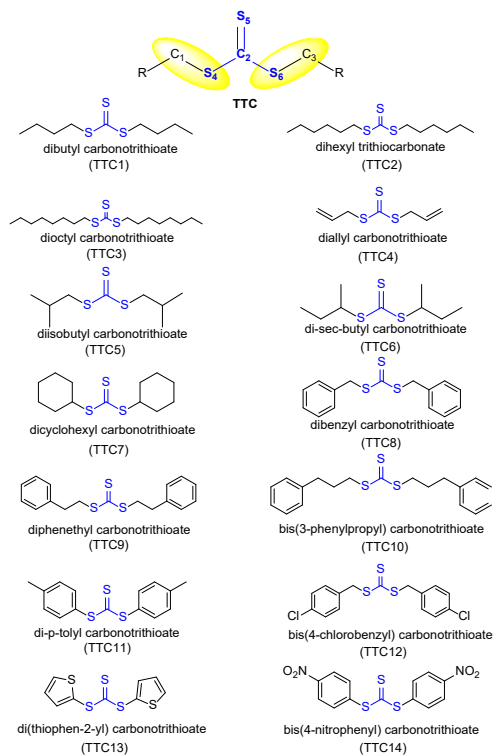


Figure 2. The general structure of TTC and studied compounds TTC1-TTC14.

2. Computational and Experimental Details

The computational studies were performed using density functional theory (DFT) with the B3LYP hybrid functional, which combines Becke's gradient correction for the exchange functional (Becke38) and the correlation functional of Lee, Yang, and Parr (LYP).³⁶ The 6-311++G(d,p) basis set was employed for all calculations³⁷⁻³⁹. The combination B3LYP/6-311++G(d,p) has consistently demonstrated close agreement with experimental results in terms of geometrical parameters, vibrational frequencies, and electronic spectra⁴⁰⁻⁴³. As a result, it ensures reliable predictions for chemical structure and reactivity, making it an ideal choice for the systems studied in this work.

Gaussian 16 software⁴⁴ was utilized for the optimization of all the molecular structures shown in **Fig. 2**, while GaussView 6 software⁴⁵ was used for geometry visualization, UV-visible spectra, IR spectra, and molecular electrostatic potential (MEP) mapping. A true global minimum on the potential energy surface is characterized by the absence of imaginary frequencies, meaning all calculated vibrational frequencies are positive. This indicates that the optimized structures lie at a stable equilibrium point without any negative curvature in the potential energy surface. The chemical structures of compounds **TTC1-TTC14** were drawn using ChemDraw.⁴⁶ The density of states (DOS) plots were generated using GaussSum 3.0 software.⁴⁷ Additionally, the HOMO

and LUMO energy levels obtained from the optimized structures were used to evaluate the chemical reactivity of the compounds. The key parameters such as chemical potential (μ), chemical softness (s), electrophilicity index (ω), and chemical hardness (η) were evaluated using the following equations,⁴⁸⁻⁵⁰

$$\text{Chemical potential } (\mu) = (IP + EA)/2$$

(1)

$$\text{Chemical hardness } (\eta) = (IP - EA)/2$$

(2)

$$\text{Chemical softness } (s) = 1/2\eta$$

(3)

$$\text{Electrophilicity index } (\omega) = \mu^2/2\eta$$

(4)

UV-visible spectra of a 10^{-5} M solution of TTCs in ethyl acetate were recorded using a Shimadzu UV-2600 spectrophotometer, covering the 200-400 nm range. FT-IR spectra were recorded in the region $500\text{--}3500\text{ cm}^{-1}$ using the Bruker Alpha II FTIR spectrophotometer.

3. RESULTS AND DISCUSSIONS

1.1. Optimization and structural analysis

The optimized symmetrical structures of substituted TTC and the bond parameters in the TTC linkage region are shown in **Figure 3**, with corresponding values in **Table 1**. The cartesian coordinates of the optimized ground state structures of **TTC1-TTC14** are presented in **Table S1-S14** and their optimized ground state energies are presented in **Table S15** in the supplementary information. Examining the C–S, and C=S bond lengths of the TTC, it is observed that the C–S and C=S bond lengths except **TTC11**, **TTC13**, and **TTC14** remain nearly unchanged, having a value of $\sim 1.769/1.770\text{ \AA}$ for C–S bond and the value $\sim 1.647\text{--}1.651\text{ \AA}$ for C=S bond. In the case of **TTC11**, and **TTC14**, the C–S bond length is

$1.792\text{ \AA}$, and in **TTC13**, it is $1.802\text{ \AA}$. The C=S bond lengths in the case of **TTC11**, **TTC13**, and **TTC14** are $1.633\text{ \AA}$, $1.624\text{ \AA}$, and $1.630\text{ \AA}$, respectively.

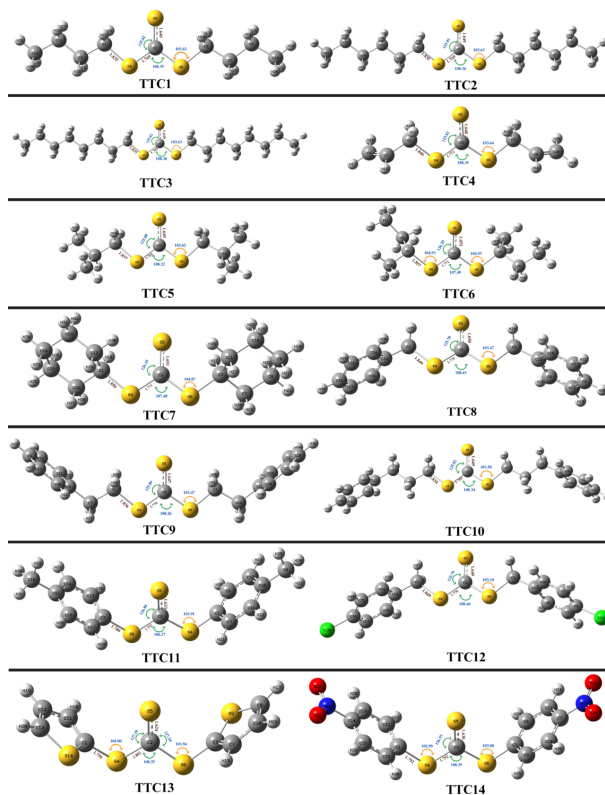


Figure 3. The optimized structures with bond lengths and bond angles of the compounds **TTC1-TTC14** in the ground state.

Interestingly, the linkage bond is strong in **TTC11**, **TTC13**, and **TTC14**, while it is weaker in the other TTCs. Apart from the bond lengths, the bond angles (S–C–S) of the TTC in **TTC11**, **TTC13**, and **TTC14** show a significant change of $\sim 2^\circ$. The bond angles in **TTC11**, **TTC13**, and **TTC14** are smaller compared to other TTCs. This indicates that the structure of TTC changes significantly when an aromatic ring is directly attached to the thiocarbonate linkage.

Table 1. The optimized bond length and bond angle in the TTC linkage region of **TTC1-TTC14** in the ground state.

Compounds	Bond Length (Å)		Bond Angle (Å)	
TTC1	C2=S5	1.649	S4-C2-S5	125.82
	C2-S6	1.769	S4-C2-S6	108.35
	C1-S4	1.835	C2-S6-C3	103.62
TTC2	C2=S5	1.649	S4-C2-S5	125.81
	C2-S6	1.769	S4-C2-S6	108.36
	C1-S4	1.835	C2-S6-C3	103.63
TTC3	C2=S5	1.649	S4-C2-S5	125.82
	C2-S6	1.769	S4-C2-S6	108.35
	C1-S4	1.835	C2-S6-C3	103.64
TTC4	C2=S5	1.648	S4-C2-S5	126.00
	C2-S6	1.771	S4-C2-S6	107.99
	C3-S6	1.846	C1-S4-C2	103.42
TTC5	C2=S5	1.649	S4-C2-S5	125.88
	C2-S6	1.769	S4-C2-S6	108.22
	C1-S4	1.837	C2-S6-C3	103.42
TTC6	C2=S5	1.651	S4-C2-S5	126.20
	C2-S6	1.771	S4-C2-S6	107.49
	C1-S4	1.857	C2-S6-C3	104.84
TTC7	C3-S6	1.856	C1-S4-C2	104.93
	C2=S5	1.651	S4-C2-S5	126.25
	C2-S6	1.771	S4-C2-S6	107.48
TTC8	C1-S4	1.850	C2-S6-C3	104.87
	C2=S5	1.650	S4-C2-S5	125.78
	C2-S6	1.770	S4-C2-S6	108.43
TTC9	C1-S4	1.849	C2-S6-C3	103.20
	C2=S5	1.647	S4-C2-S5	125.86
	C2-S6	1.770	S4-C2-S6	108.26
TTC10	C1-S4	1.836	C2-S6-C3	103.47
	C2=S5	1.649	S4-C2-S5	125.82
	C2-S6	1.769	S4-C2-S6	108.34
TTC11	C1-S4	1.834	C2-S6-C3	103.50
	C2=S5	1.633	S4-C2-S5	126.86
	C2-S6	1.792	S4-C2-S6	106.27
TTC12	C1-S4	1.789	C2-S6-C3	103.91
	C2=S5	1.649	S4-C2-S5	125.79
	C2-S6	1.770	S4-C2-S6	108.40
TTC13	C1-S4	1.849	C2-S6-C3	103.10
	C2=S5	1.624	S4-C2-S5	127.18
	C2-S6	1.802	S6-C2-S5	127.24
TTC14	C2-S4	1.802	S4-C2-S6	105.56
	C1-S4	1.756	C2-S6-C3	104.00
	C3-S6	1.756	C1-S4-C2	103.94
TTC14	C2=S5	1.630	S4-C2-S5	126.93
	C2-S6	1.792	S4-C2-S6	106.12
	C1-S4	1.792	C2-S6-C3	103.00
	C3-S6	1.792	C1-S4-C2	102.99

1.2. Natural population analysis

Natural Population Analysis (NPA)^{48,49} was conducted using natural atomic orbital occupancy based on the concept of Natural Bond Orbitals (NBO)⁵¹ implemented in the Gaussian program to determine the natural charges on the atoms of substituted trithiocarbonates (**TTC1-TTC14**). **Figure 4** presents the histogram plot of the natural atomic charge on the atoms of the TTCs linkage group. The plot illustrates the impact of

different substitutions on the TTC group by analyzing the charge distribution across its atoms. S4 and S6 are the terminal atoms of TTC through which the linkage with various substituted groups is attached. C1 and C3 belong to the atom on the other side of the linkage bond. S1 and S3 are the TTC group's terminal atoms that link to various substituted groups. C1 and C3 are the atoms on the linkage bond's opposite side. C1 and S4 are the atoms involved in the C=S bond in the TTC group. The NPA shows that the charges on atoms C1, C2, and

C3 are negative, while S4 and S6 carry positive charges. In TTC11, TTC13, and TTC14, the charge on atom S5 shifts from negative to positive, indicating that these compounds become nucleophilic, whereas the TTC group remains electrophilic in the other cases. The structures TTC4, TTC6, TTC7, TTC11, TTC13, and TTC14 exhibit notable variations in the charge distribution within the TTC group. The bond lengths of the C-S linkage, as shown in Table 1, indicate that the linkage bond weakens in TTC4, TTC6, TTC7, TTC8, and TTC12, while it strengthens in TTC11, TTC13, and TTC14.

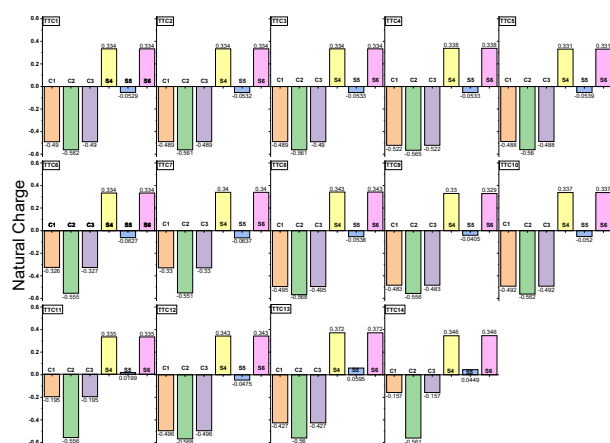


Figure 4. Histogram plot of natural atomic charge on the atoms of TTCs linkage group.

1.3. Frontier Molecular Orbitals Analysis and Density of State

The reactivity of conjugated systems was evaluated through the analysis of frontier molecular orbitals (FMOs), specifically the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), and their energy gap (E_g). This analysis identifies the most reactive centers in the molecule, aiding in the prediction of electrophilic

and nucleophilic attack sites in various reactions.⁵² A lower energy gap indicates reduced kinetic stability and enhanced chemical reactivity. HOMO and LUMO orbitals of **TTC1** – **TTC14** computed using DFT method B3LYP/6-311++G (d, p) are shown in **Fig. 5**, and the energies of HOMO and LUMO along with the band gap are presented in **Table 2**. As shown in **Fig. 5**, the HOMO is predominantly localized on the C–S bond in all TTC compounds, while the LUMO, except in **TTC14**, is mainly concentrated at the sulfur atom. The energy gap (E_g) between the HOMO and LUMO is highest in **TTC8**, around 5.26 eV, indicating its high stability. In contrast, **TTC14** has the lowest gap at approximately 3.52 eV, reflecting its higher chemical reactivity due to the presence of electron-withdrawing group. This increased reactivity in **TTC14** is evident in the HOMO and LUMO plots, which clearly show charge transfer from the trithiocarbonate moiety to the substituent group. A molecule that is harder, more stable, and less reactive tends to have a larger energy band gap between its HOMO and LUMO. The subsequent charge transfer interactions within the molecules caused the decreased value of the HOMO and LUMO energy gap.

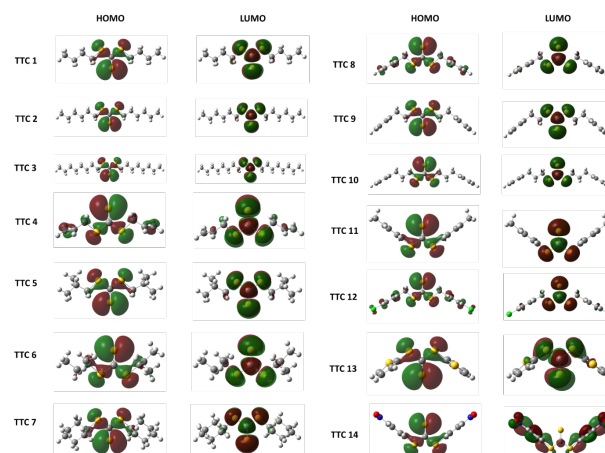


Table 2. Calculated value of the global chemical reactivity indices of **TTC1-TTC14** compounds.

Compound	HOMO (eV)	LUMO (eV)	E_g (eV)	μ (eV)	η (eV)	S (eV)	ω (eV)
TTC 1	-6.18	-1.87	4.30	-4.03	2.15	0.23	3.77
TTC 2	-6.16	-1.86	4.30	-4.01	2.15	0.23	3.74
TTC 3	-6.16	-1.85	4.30	-4.01	2.15	0.23	3.73
TTC 4	-6.33	-2.05	4.28	-4.19	2.14	0.23	4.11
TTC 5	-6.17	-1.87	4.31	-4.02	2.15	0.23	3.76
TTC 6	-6.22	-1.92	4.30	-4.07	2.14	0.23	3.85
TTC 7	-6.17	-1.88	4.29	-4.02	2.14	0.23	3.78
TTC 8	-6.24	-1.98	5.26	-4.11	2.13	0.23	3.96
TTC 9	-6.24	-1.95	4.29	-4.09	2.14	0.23	3.90
TTC 10	-6.25	-1.94	4.31	-4.09	2.15	0.23	3.90
TTC 11	-6.06	-1.84	4.21	-3.95	2.10	0.24	3.70
TTC 12	-6.43	-2.19	4.24	-4.31	2.12	0.24	4.39
TTC 13	-6.35	-2.17	4.19	-4.26	2.09	0.24	4.34
TTC 14	-6.91	-3.38	3.52	-5.15	1.76	0.28	7.53

Figure 5. HOMO and LUMO plots of the synthesized (**TTC1-TTC14**) compounds through B3LYP/6-311++G (d,p) level of theory.**Figure 6.** Calculated DOS plots of substituted trithiocarbonates (**TTC1-TTC14**).

compounds (**TTC1-TTC14**) are plotted and displayed in **Figure 6**. It offers a visual depiction of the density of molecular orbitals and how they affect chemical bonding study.⁵³ The GaussSum 3.0 program⁴⁷ is used to plot DOS in terms of Mulliken population analysis by convoluting the molecular orbital information using full width at half maximum (FWHM) of 0.3 eV. The analysis provides insights into the distribution of electronic states across different energy levels, particularly HOMO-LUMO gap in molecular systems. For the trithiocarbonate linkages, the DOS analysis helps identify the contributions of various molecular orbitals to the overall electronic structure, and how these are affected by substituent variations. By comparing the DOS profiles of the substituted trithiocarbonate, it is observed that there are shifts in HOMO and LUMO energy levels to lower the energy in the presence of substituents chlorobenzyl, thiophenyl, and nitrophenyl, which lead to lower the band gap in **TTC12**, **TTC13**, and **TTC14** indicating the increase in compounds reactivity.

Density of States (DOS) plots of the

1.4. Global Chemical Reactivity

Analysis

The global chemical reactivity of trithiocarbonates (TTCs) was systematically examined using quantum chemical descriptors derived from frontier molecular orbitals (HOMO and LUMO) and other DFT-based parameters. This analysis provides insights into the reactivity patterns of TTCs, particularly in electron transfer processes and bond dissociation reactions across various chemical environments. According to Koopmans,⁵⁴ and Kohn–Sham theorem,⁵⁵ the global chemical reactivity descriptors of molecules, such as hardness, chemical potential, softness, electronegativity, and electrophilicity index, as well as local reactivity, can be characterized using the HOMO and LUMO energy values of a molecule. HOMO represents the ability to donate an electron (nucleophile), and its energy is directly related to the ionization potential (IP). In contrast, LUMO represents the inclination to gain an electron (electrophile), and its energy is directly related to electron affinity (EA). The quantum chemical parameters, including HOMO, LUMO, energy gap, ground state energy, chemical potential (μ), global hardness (η), softness (s), and global electrophilicity (ω), have been computed by DFT method B3LYP/6-311++G(d,p) are given in **Table 2**. The chemical potential provides a global reactivity index and is related to charge transfer from a system of higher chemical potential to lower chemical potential. The highest chemical potential in **TTC14** is around -5.15 eV, indicating its higher chemical reactivity. In contrast, **TTC11** has a chemical potential of approximately -3.95 eV, reflecting its lower chemical reactivity.

Chemical hardness (η) and softness (S) efficiently estimate organic moiety's reactivity and stability⁵⁶. The molecules with less hardness (η) and greater softness (S) values have strong electron-acceptance and good electrophile species. Softness has an inverse relation with twice the value of hardness. For a molecule to be reactive, the value of “ S ” should be larger, and the “ η ” value should be lower, indicating the increasing electron acceptance ability. For a molecule to be stable, the value of “ S ” should be smaller, and the “ η ” value should be larger. The compound **TTC14** shows high softness (0.28 eV) and low hardness (1.76 eV), indicating its higher chemical reactivity.

Organic compounds can be classified organic molecules based on their electrophilic behavior using the electrophilicity index (ω) scale.^{57, 58} Molecules are categorized as strong electrophiles with $\omega \geq 1.5$ eV, moderate electrophiles with $0.8 \leq \omega < 1.5$ eV, and marginal electrophiles with $\omega < 0.8$ eV. Only strong electrophiles participate in experimental reactions. Also, super-electrophiles are species with $\omega \geq 4.0$ eV^{59, 60} showing high reactivity in polar reactions^{61, 62}. The electrophilic index of compounds **TTC1–TTC11** falls between 1.5 eV and 4.0 eV, indicating high reactivity. In contrast, compounds **TTC12**, **TTC13**, and **TTC14** have electrophilic indices of 4.39 eV, 4.34 eV, and 7.53 eV, respectively, surpassing 4.00 eV, classifying them as super-electrophilic with very high reactivity.

1.5. Molecular Electrostatic Potential (MEP) Analysis

The molecular electrostatic potential

(MEP) was analyzed to visualize the electrostatic distribution of electrons and nuclei, aiding in the identification of reactive sites in chemical reactions. This analysis highlights regions prone to electrophilic and nucleophilic attacks, as well as potential hydrogen bonding interactions relevant to biological processes.⁶³

The MEP plots serve as valuable visual tools for understanding the compound's reactive centers and polar regions. **Figure 7** presents the 3D molecular electrostatic potential (MEP) plots for each TTC compound, optimized at the B3LYP/6-311++G(d,p) level of theory, to identify favorable sites for nucleophilic and electrophilic attacks. The plot's surface regions are arranged in the hierarchical order: red < orange < yellow < green < blue. The blue zones, indicating electron deficiency, are more likely to correspond to electrophilic sites, while the red zones, representing electron-rich areas, particularly around oxygen atoms, highlight nucleophilic sites. Green represents neutral or zero potential regions, typically indicating a balance between positive and negative extremes.

Orange and yellow indicate intermediate potentials, with orange marking slightly electron-rich areas and yellow highlighting moderately electron-poor regions. The map's color code falls within the range of the map's regions of $-0.03 \text{ e}/\text{\AA}$ dark red and $+0.03 \text{ e}/\text{\AA}$ dark blue.

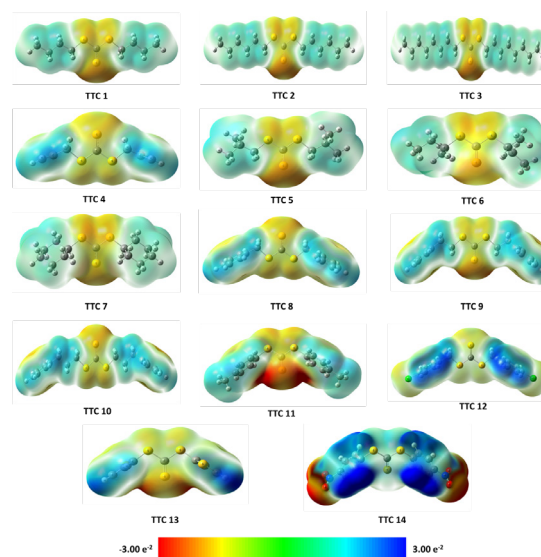


Figure 7. Molecular Electrostatic Potential (MEP) plot of **TTC1-TTC14** compounds.

The MEP plot in **Fig. 7** reveals an electrophilic region near the terminal sulfur atom of the C=S bond in **TTC1-TTC13**. In **TTC11**, the sulfur atom is particularly susceptible to electrophilic attack, while in the other compounds, the susceptibility is moderate. For **TTC13**, a nucleophilic region is also observed near the C-H bond of the thiophene ring. As predicted earlier, **TTC14**, which exhibits high reactivity, shows a strong electrophilic region near the oxygen atom of the nitro group and nucleophilic regions near the C-H bonds of the phenyl ring in the MEP plot.

1.6. Absorption spectra analysis

The UV-visible absorption spectra of the synthesized TTC compounds (**TTC2-TTC6**, **TTC8**, **TTC9**, and **TTC12**) were recorded to investigate the effect of substituents on their excitation profiles. To further characterize the electronic transitions, the UV-visible spectra for all

substituted TTCs (TTC1-TTC14) were calculated using time-dependent density functional theory (TD-DFT) at the B3LYP/6-311++G(d,p) level of theory. **Figure 8** presents a comparison of the experimental and theoretical spectra.

Table 3 summarizes the key results, including absorption wavelengths (λ_{abs}), excitation energies (E_{opt}), oscillator strengths, and the major contributions of molecular orbital transitions. The theoretical UV spectra calculated using DFT show excellent agreement with the experimentally measured absorption

wavelengths.

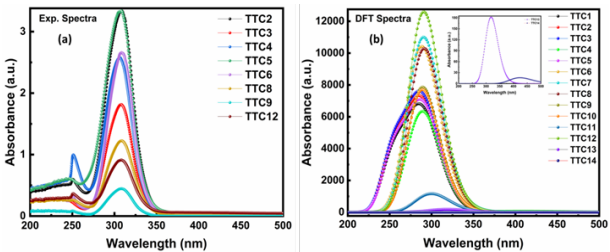


Figure 8. (a) Experimental absorption spectra **TTC2-TTC6**, **TTC8**, **TTC9**, and **TTC12** compounds and (b) calculated UV-visible spectra of **TTC1-TTC14** at DFT/B3LYP/6-311++G(d,p) level of theory.

Compounds	λ_{abs}^{exp} (nm)	Transitions	λ_{abs}^{DFT} (nm)	E_{opt} (eV)	Oscillator Strength	Major contributions
TTC1	-	$S_0 \rightarrow S_1$	411.46	3.01	0	H→L (100%)
		$S_0 \rightarrow S_2$	289.16	4.29	0.1525	H-2→L (91%)
		$S_0 \rightarrow S_3$	255.63	4.85	0.932	H→L+1 (89%)
TTC2	309.0 250.5	$S_0 \rightarrow S_1$	411.50	3.01	0	H→L (100%)
		$S_0 \rightarrow S_2$	289.33	4.29	0.1644	H-2→L (91%)
		$S_0 \rightarrow S_3$	255.52	4.85	0.1009	H→L+1 (99%)
TTC3	308.0 244.5	$S_0 \rightarrow S_1$	411.50	3.01	0	H→L (100%)
		$S_0 \rightarrow S_2$	289.37	4.29	0.1709	H-2→L (91%)
		$S_0 \rightarrow S_3$	255.53	4.85	0.1048	H→L+1 (89%)
TTC4	305.8 251.2	$S_0 \rightarrow S_1$	410.67	3.02	0.0015	H→L (99%)
		$S_0 \rightarrow S_2$	290.40	4.27	0.1486	H-2→L (91%)
		$S_0 \rightarrow S_3$	270.33	4.59	0.0147	H→L+1 (93%)
TTC5	308.5 246.5	$S_0 \rightarrow S_1$	411.02	3.02	0	H→L (100%)
		$S_0 \rightarrow S_2$	290.41	4.27	0.1594	H-2→L (91%)
		$S_0 \rightarrow S_3$	256.20	4.84	0.0988	H→L+1 (89%)
TTC6	308.4 250.2	$S_0 \rightarrow S_1$	409.39	3.03	0.0003	H→L (99%)
		$S_0 \rightarrow S_2$	293.13	4.23	0.1643	H-2→L (93%)
		$S_0 \rightarrow S_3$	280.69	4.42	0.1068	H-1→L (93%)
TTC7	-	$S_0 \rightarrow S_1$	409.74	3.03	0.0004	H→L (99%)
		$S_0 \rightarrow S_2$	294.60	4.21	0.1855	H-2→L (93%)
		$S_0 \rightarrow S_3$	282.27	4.39	0.0994	H-1→L (94%)
TTC8	308.5 250.5	$S_0 \rightarrow S_1$	413.64	3.00	0	H→L (98%)
		$S_0 \rightarrow S_2$	292.42	4.24	0.2277	H-2→L (92%)
		$S_0 \rightarrow S_3$	282.21	4.39	0.0302	H→L+1 (95%)
TTC9	308.1 250.2	$S_0 \rightarrow S_1$	413.18	3.00	0	H→L (100%)
		$S_0 \rightarrow S_2$	289.23	4.29	0.1941	H-2→L (90%)
		$S_0 \rightarrow S_3$	271.54	4.57	0	H-3→L (99%)
TTC10	-	$S_0 \rightarrow S_1$	410.92	3.02	0	H→L (100%)
		$S_0 \rightarrow S_2$	289.14	4.29	0.1904	H-2→L (91%)
		$S_0 \rightarrow S_3$	271.04	4.58	0	H-3→L (100%)
TTC11	-	$S_0 \rightarrow S_1$	420.04	2.95	0	H→L (100%)
		$S_0 \rightarrow S_2$	301.53	4.11	0	H-2→L (99%)
		$S_0 \rightarrow S_3$	299.96	4.13	0.0288	H-3→L (32%)
TTC12	308.0 251.0	$S_0 \rightarrow S_1$	414.02	3.00	0	H→L (97%)
		$S_0 \rightarrow S_2$	291.82	4.25	0.2436	H-2→L (92%)
		$S_0 \rightarrow S_3$	286.77	4.32	0.0692	H→L+1 (95%)
TTC13	-	$S_0 \rightarrow S_1$	432.11	2.87	0	H→L (100%)
		$S_0 \rightarrow S_2$	321.21	3.86	0.0003	H-2→L (10%)
		$S_0 \rightarrow S_3$	318.29	3.90	0.0042	H→L+1 (93%)
TTC14	-	$S_0 \rightarrow S_1$	424.20	2.92	0	H→L+2 (100%)
		$S_0 \rightarrow S_2$	423.57	2.93	0.0004	H→L (99%)
		$S_0 \rightarrow S_3$	397.94	3.12	0	H→L+1 (99%)

The calculated UV-visible spectra indicate that the transition to the first excited state (S1, HOMO→LUMO) is theoretically possible but contributes minimally to the overall absorption intensity due to its zero-oscillator strength, which aligns with experimental observations. The absorption spectra reveal a strong absorption peak around 308 nm and a weaker one near 250 nm, primarily corresponding to HOMO-2→LUMO and HOMO→LUMO+1 transitions in most cases, except for **TTC9**, **TTC10**, **TTC13**, and **TTC14**. This variation can be explained by the DOS plot, which shows that, instead of the HOMO→LUMO+1 transition, the HOMO-3→LUMO transition is possible due to the high density of states near lower energy levels. Additionally, **TTC13** and **TTC14** exhibit significantly weaker absorption theoretically, attributed to a substantial downward shift in the energies of their HOMO and LUMO states.

1.7. Bond dissociation Enthalpies and Gibbs free energies of TTC linkage bond

The thermodynamic stability of TTC terminal bonds (C-S) can be effectively evaluated by analyzing two critical parameters: Bond Dissociation Enthalpies (BDE) and Gibbs Free Energies (ΔG) of the bonds C1-S4 and C3-S6, as shown in **Figure 2**. These thermodynamic parameters provide insight into the strength of TTC linkages with various substituents. The calculated BDEs and Gibbs free energies for the TTC linkage bonds are summarized in **Table 4**, offering a quantitative measure of bond stability across different molecular configurations.

Table 4. Bond Dissociation Enthalpies and Gibbs Free Energies of TTC linkage bond calculated at B3LYP/6-311++G(d,p) level of theory.

COMPOUNDS	BDE (KCAL/MOL)	ΔG (K C A L / MOL)
TTC1	59.84	-45.93
TTC2	59.94	-45.97
TTC3	59.99	-46.19
TTC4	44.17	-32.06
TTC5	59.10	-45.71
TTC6	56.56	-42.27
TTC7	57.59	-43.98
TTC8	47.22	-35.10
TTC9	60.07	-46.71
TTC10	59.65	-45.99
TTC11	70.65	-58.02
TTC12	46.68	-34.51
TTC13	75.67	-62.60
TTC14	69.09	-57.19

The high BDE values and Gibbs free energies for **TTC11**, **TTC13**, and **TTC14** suggest a strong linkage with their substituents. In contrast, **TTC4**, **TTC8**, and **TTC12** exhibit lower BDE values and Gibbs free energies, indicating a weaker linkage. The remaining compounds show moderate linkage strength with their respective substituents. It is notable that the linkage is stronger when a substituent with a ring structure, such as tolyl, thiophenyl, or nitrophenyl, is directly attached to the TTC linkage without an alkyl spacer, as observed in **TTC11**, **TTC13**, and **TTC14**.

1.8. Vibrational analysis

To examine the effect of the attached group on the vibrational features of trithiocarbonates, a vibrational analysis

of substituted TTCs was conducted using the DFT method at the B3LYP/6-311++G(d,p) level of theory. Infrared spectroscopy is used to determine the functional groups present in organic compounds to identify the characteristic vibrations such as stretching, bending, and twisting^{64, 65}. **Figure 9** shows the computed IR spectra for **TTC1–TTC14** in the 500–3500 cm^{-1} range, while **Figure 10** presents the experimentally recorded FT-IR spectra of the synthesized trithiocarbonates **TTC2–TTC6**, **TTC8**, **TTC9**, and **TTC12** within the same spectral region.

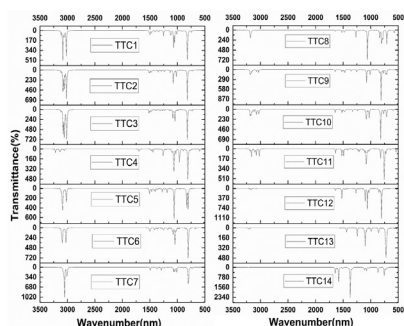
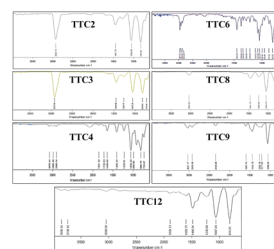


Figure 9. Computed IR spectra of selected compounds **TTC2**, **TTC3**, **TTC4**, **TTC6**, **TTC8**, **TTC9**, and

TTC12 at B3LYP/6-311++G (d, p) level of theory.

The theoretical and experimental FT-IR spectra show a strong resemblance, confirming the computational accuracy. A strong band in the region 600–900 cm^{-1} corresponds to the –S–C–S– in-plane bending vibration TTC group. The band appeared in the region 900–1200 cm^{-1} corresponds to the stretching vibration of the carbon-sulfur double bond (C=S) present in the TTC group. It is observed in the theoretically calculated IR spectra that the carbon-sulfur (C–S) single bond stretching vibration is very weak, appearing in the range of 400–600 cm^{-1} . Therefore, it is not visible in the FT-IR spectra. The appearance of C–S stretching, C=S stretching, and –S–C–S– in-plane bending vibrations in substituted TTCs are presented in **Table 5**.



Compounds	C-S str. (cm^{-1})		S-C-S (cm^{-1}) (in-plane)		S-C-S (cm^{-1}) (out-of-plane)		C=S str. (cm^{-1})	
	Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal
TTC1	-	531	-	816.98	-	475.61	-	1069.06
TTC2	-	534.02	819.48	818.18	-	473.70	1054.68	1074.92
TTC3	-	536.57	820.03	818.14	-	473.27	1055.24	1082.39
TTC4	-	518.99	808.73	808.48	-	476.05	1054.20	1063.84
TTC5	-	530.40	-	829.94	-	472.71	-	1059.44
TTC6	-	530.60	808.25	802.11	-	474.78	1054.72	1044.45
TTC7	-	529.14	-	800.83	-	473.26	-	1048.45
TTC8	-	508.90	807.90	800.64	-	476.12	1052.72	1059.51
TTC9	-	530.63	816.70	811.95	-	475.10	1058.03	1076.10
TTC10	-	530.30	-	817.75	-	474.47	-	1080.09
TTC11	-	538.07	-	753.77	-	471.00	-	1080.46
TTC12	-	530.38	816.25	803.07	-	475.65	1067.24	1060.38
TTC13	-	483.14	-	726.47	-	469.99	-	1097.72
TTC14	-	525.44	-	755.00	-	465.08	-	1078.78

Figure 10. FTIR spectra of synthesized compounds **TTC2**, **TTC3**, **TTC4**, **TTC6**, **TTC8**, **TTC9** and **TTC12**

Table. 5 Calculated and experimental vibrational frequencies of some prominent wavenumbers (cm^{-1}) of **TTC1-TTC14** Compounds

3. Conclusions

Trithiocarbonate (TTC) linkages are pivotal in polymerization reactions, creating materials with specific properties. This study presents a comprehensive theoretical investigation into the impact of substituents on TTC linkages, focusing on their electronic structure, stability, and reactivity using the powerful Density Functional Theory (DFT) approach. Key electronic parameters, such as the HOMO, LUMO, and the energy gap, were analyzed to assess the molecular stability and potential reactivity of various substituted TTCs. Additionally, UV-visible absorption and IR spectroscopy were employed to characterize these compounds. The molecular electrostatic potential (MEP) analysis was conducted to identify nucleophilic and electrophilic regions, while the density of states (DOS) provided additional insights into the electronic distribution. Stability and reactivity were evaluated using global reactivity descriptors. The electrophilic index for compounds **TTC1–TTC11** ranges from 1.5 eV to 4.0 eV, indicating high reactivity. In contrast, compounds **TTC12**, **TTC13**, and **TTC14** are classified as super-electrophilic, exhibiting extremely high reactivity. The MEP plot reveals that the terminal sulfur atom of the C=S bond in **TTC11** is prone to electrophilic attack, while **TTC13** shows a nucleophilic region

near the C-H bond of the thiophene ring. **TTC14**, known for its high reactivity, displays a strong electrophilic region near the oxygen atom of the nitro group and nucleophilic regions near the C-H bonds of the phenyl ring.

Furthermore, high bond dissociation energy (BDE) values and Gibbs free energies for **TTC11**, **TTC13**, and **TTC14** indicate a strong TTC linkage with their substituents. In contrast, **TTC4**, **TTC8**, and **TTC12**, which have lower BDE values and Gibbs free energies, demonstrate weaker substituent linkages. The linkage is stronger when a substituent with a ring structure, such as tolyl, thiophenyl, or nitrophenyl, is directly linked to the TTC linkage without an alkyl spacer, as shown in **TTC11**, **TTC13**, and **TTC14**. These findings provide valuable insights into the reactivity, stability, and potential biological activity of substituted TTCs, offering a solid foundation for designing compounds with tailored properties using advanced DFT methodologies.

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Declarations

Competing interests

The authors disclose no conflicts of interest relevant to this study's content.

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Data Availability

The authors confirm that all relevant data are included in the article.

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