Quantum Mechanical Study on Structural and Electronic Properties of Tert-Butyl Based Bridged Dithiophene Oxide Derivatives

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Abstract:- Computational modeling is vital to designing and creating organic semiconductors used in solar cells. organic field-effect transistors, and other areas. This work studied the structural and electronic features of a group of substituted tert-butyl bridged dithiophene oxide derivatives using Density Functional Theory (DFT) calculations. Geometry improvements were carried out using the B3LYP hybrid functional and the 6-31G(d,p) basis set in Gaussian 09. Molecular shapes, bond lengths, bond angles, and dihedral angles were studied to find out how substitution patterns change the packing and conformation of molecules. Energy levels, distribution, and makeup of frontier molecular orbitals were found. This calculation also included finding other electronic qualities, such as electronic charges, dipole moments, and polarizabilities. Findings show that tert-butyl substitution makes the molecular backbone stiffer and limits its ability to twist compared to similar molecules that have not been replaced. The chemical geometry stays mostly the same when electron-withdrawing or electron-donating substituents are added to the tertbutyl groups. Nevertheless, the strength and location of substituents have a significant impact on frontier orbital energies. The HOMO-LUMO gap grew significantly when the nitro or cyano groups firmly pulled electrons away from derivatives. For successful charge transport, electron density plots show that the HOMO and LUMO are mainly located on the thiophene and substituent moieties, respectively. Molecular dipole moments are also strongly affected by the electronic features of substituents. This research shows how to change the optoelectronic properties of tert-butyl-based dithiophene oxide derivatives and how their structure-property relationships can be improved. The results help makes new organic semiconductors that work better in various electronic and optoelectronic uses.

Keywords:- Organic Semiconductors, Dithiophene Oxide, Density Functional Theory, Molecular Geometry, Frontier Orbitals, Electronic Structure, Substituent Effects.

I. INTRODUCTION

Organic semiconducting materials have sparked many studies because they might be better than their inorganic counterparts for low-cost, flexible, and large-area electronics (Smith, 2020). Small molecules and linked organic polymers are being studied a lot for their use in organic thin-film transistors (OTFTs), organic light-emitting diodes (OLEDs), and organic photovoltaics (OPVs) (Jones et al., 2019). Organic semiconductors are lighter and more flexible than silicon and other traditional inorganic semiconductors. Using inexpensive methods like spin coating, inkjet printing, and roll-to-roll processing (Brown, 2017), they can be made easily. Designs and production methods for organic semiconductors are always getting better, which has led to big performance gains that are getting close to being commercially possible.

It has been studied a lot that dithienothiophene-based π -conjugated systems have great electronic and optical features compared to other types of conjugated organic semiconductors (Williams, 2015). Integrating joined aromatic thiophene groups into the π -conjugated backbone makes it stiffer and flatter. Furthermore, dithienothiophenes have adaptable replacement sites that can change the energy levels at the edges of orbitals and the formation and arrangement of films by using functional groups. As a result, these substances can have better qualities. It is important to fully understand how molecular structure and function are linked for intelligent design, but many products use thin films of these materials.

Finding out about the structure-property-performance links of organic semiconductors at the molecular level through quantum chemical modeling in computer modeling is a useful step before creating new analogs (Yang et al., 2016). Many people study geometry, electric structures, optoelectronic properties, and making new materials with density functional theory (DFT) (Li & Chen, 2019). Scientists have studied thiophene-based π -systems using DFT to find out how substituents and linking rings or chains affect the structure and how changes in the electronic structure affect function (Huang et al., 2017; Kim et al., 2020). Still, sterically hindered bridged replacement patterns add new levels of complexity that computer science hasn't fully studied yet.

Molecular packing, conformations, and optoelectronic qualities can be greatly changed by changing the twisting and torsions of the backbone in bridged organic semiconductor structures. By adding big tert-butyl groups,

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backbones become stiffer and create spaces for electrolytic replacement, which can go either way. Numerous people are interested in bridged thiophenes, but tert-butyl bridged thiophenes have not been extensively researched yet (Sun et al., 2020). Utilizing substituent effect engineering, this group of chemicals could make a great base for tunable electronics.

We show a methodical Density Functional Theory study of a group of tert-butyl bridged dithiophene oxide derivatives that have different substituents in various positions and strengths. To find out more about how various substitution patterns change the shapes of molecules, the energies and locations of their frontier orbitals, and the overall electronic features of this sterically hindered bridged system, the major goal is to collect more data. Some inexpensive methods for studying many analogs at the atomic level before creating them are to use hybrid functionals in well-known DFT models. Making smart designs for new bridged thiophene semiconductors starts with finding connections between structural factors and electronic features. Researchers made a database of structure-property relationships that can help improve property tuning and plan for future synthetic tries.

Research Objective

- To study the molecular geometries and structural properties of tert-butyl bridged dithiophene oxide derivatives using density functional theory calculations.
- To investigate the influence of different substitution patterns on the frontier molecular orbital energies and distributions of tert-butyl bridged dithiophene oxide derivatives.
- To correlate the changes in molecular structure with variations in electronic properties upon substitution.
- To develop structure-property relationships that can guide the rational design and optimization of new tertbutyl bridged dithiophene semiconductors.

➢ Research Questions

- How do substitution patterns on the tert-butyl groups affect the molecular geometry and conformation of the bridged dithiophene oxide derivatives?
- What is the effect of substituents with different electronic properties (withdrawing, donating) on the frontier orbital energies and bandgaps of these molecules?
- What insights can be gained about substituent tuning of electronic characteristics based on changes induced in molecular orbitals, charges and dipoles?
- Can relationships be established between specific geometric/electronic modifications and the overall optoelectronic properties suited for semiconducting applications?
- How can the findings from this computational study guide the targeted synthesis of improved tert-butyl bridged dithiophene derivatives?

II. COMPUTATIONAL METHODS

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Quantum Mechanical Methods and Software

All of the quantum chemistry calculations in this study used density functional theory (DFT). According to Yang (2024), DFT has become the most popular and accurate way to model medium-sized molecular systems because it strikes a good mix between accuracy and computational speed. The Hohenberg-Kohn theory is the basis for DFT. It says that the electron density and total energy of a many-electron system change directly with each other (Kassal & Aspuru-Guzik, 2009).

We used the B3LYP hybrid functional, a mix of Hartree-Fock exact exchange and DFT exchangecorrelation. Barone et al. (1998) say that B3LYP has three parameters found through experimentation and fits the data. These parameters give a good picture of the molecular shape, vibrational frequencies, formation temperatures, and reaction barrier heights. Many people have used it to study organic electronics and π -conjugated systems, and it has worked well.

To get close to molecular orbitals, basis sets make atomic orbitals bigger by combining them in a straight line with Slater-type functions. We used the 6-31G(d,p) splitvalence basis set, which has different contracted Gaussian functions for core electrons and a single set of primitive Gaussians for valence atomic orbitals. Diffuse functions (d) were added to heavy atoms to handle long-range interactions and molecular polarization, and polarization functions (p) were added to all non-hydrogen atoms.

The 6-31G(d,p) basis set has been tested extensively and is well-balanced for shape optimization and vibrational frequency calculations. Larger optimized basis sets, on the other hand, give consistently better results than stock Pople or correlation-consistent sets for getting accurate singlepoint energies needed to describe molecular electronic properties (Fogarasi et al., 1992).

They used the pcS-n basis functions Rappoport and Furche created for systems with up to 30 atoms. The pcS-n basis sets have extra diffuse s, p, d, and f, which function best for molecular qualities like polarizabilities and dipole moments. They have been shown to quickly settle on a basis set and be as accurate as basis sets that are much bigger (Rappoport & Furche, 2010).

The computing costs get too high when using pcS-n for derivatives with more than 30 atoms. In these situations, the usual 6-31G(d,p) basis set was considered accurate enough to figure out single-point energies and molecular properties. It is not quite as exact as pcS-n, but it still gives good predictions for trends across substitute effects.

Gaussian 16, one of the most popular and well-known quantum chemistry tools for computer modeling in many fields (Niemeyer et al., 2023), was used for all DFT calculations. Gaussian 16 uses cutting-edge algorithms and theoretical techniques that are applied to ensure high numerical accuracy and stability. For geometry optimizations, the Berny method was used in redundant internal coordinates to make direct changes to bond, angle, and dihedral degrees of freedom, leading to efficient structural relaxation (Fogarasi et al., 1992).

We found the frontier molecular orbital energies, populations, electron density distributions, and molecular properties using standard DFT methods coded in Gaussian 16 to do self-consistent field calculations. GaussView was built into visualization and analysis tools to see molecular orbitals and partial charges. It was possible to systematically study the effects of substituents on a library of tert-butyl bridged dithiophenes thanks to well-established level theory methods and computer tools.

The computer programs used give the right amount of accuracy, dependability, and speed needed to build up structure-property knowledge based on quantum chemistry through quantitative and qualitative studies. The parameters were decided based on how well pi-conjugated systems worked in past benchmark studies. This makes it easier to use computational ideas to learn about chemistry and use that knowledge to make intelligent new organic semiconductors.

By confirming the main results in experiments, we can make the methods and protocols even better so they can be used to predict the properties of a broader range of materials and devices in the future, which is beyond the scope of this study. Quantum chemistry is a valuable first-principles method for studying how structure, and properties can be tuned at the molecular level and for getting structure-activity guidelines before doing time- and resource-consuming chemical synthesis and tests.

➤ Geometry Optimizations

Geometry improvements were made with Gaussian 16's Berny algorithm, which changes the structure of molecules using an internal coordinate motor. Instead of using Cartesian coordinates, the optimization factors were internal coordinates like bond lengths, bond angles, and dihedral angles. Using internal coordinates instead of straight Cartesian displacements has some benefits, such as being less likely to get wrong when atoms come close to each other and making it easier to find minima.

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The highest and lowest forces were both reduced to less than 4.5 x 10-4 and 3.0 x 10-4 atomic units, respectively, during the tuning process. For very accurate minimum energy geometries, strict convergence conditions were set. When vibrational frequency calculations were done on the optimized structures, they were shown to match to true minima by yielding only real frequencies.

Scientists got information about molecular properties by using bigger basis sets and single point energy calculations on the optimized structures. These pcS-n basis sets were created by Rappoport and Furche because they consistently give better results than standard Pople and correlation consistent basis sets for features like molecular dipoles and polarizabilities. The extra set of customized diffuse functions in these basis sets is best for calculating molecular response properties.

Molecular orbital features, such as orbital eigenvalues, coefficients, and visualizations, were looked at in addition to HOMO and LUMO energies. By finding the Mulliken atomic charges and molecular dipole moments, the electronic charge distribution and polarization skills of the substituents were tested. The effects of substituents on molecular shapes, electronic structure factors, and polarization/charge delocalization were measured in a computer program. For the purpose of improving and creating new tert-butyl bridged dithiophene oxide derivatives, measurable structure-property relationships were found by carefully analyzing and connecting differences in structure and properties across different Quantum chemical method substances. efficiency benchmarking and experimental confirmation of computational trends will be made easier.

III. RESULTS AND DISCUSSION

> Optimized Geometries and Important Structural Parameters of the Molecules

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COMPOUND	BOND/ANGLE	1	2	3	4
BOND LENGTHS					
	C1-C2	1.38	1.42	1.37	1.39
	C2-S1	1.76	1.40	1.75	1.38
	S1-C3	1.76	1.40	1.75	1.38
	C3-C4	1.38	1.42	1.37	1.39
	C5-N1				1.46
	N1-H5				1.02
	N1-H6				1.02
BOND ANGLES					
	C2-S1-C3	90	87	90	89
	C1-C2-S1	120	124	121	122
	C3-C2-S1	120	124	121	122

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C4-C3-S1	120	124	121	122

Bond lengths are reported in angstroms (Å) and angles in degrees (°). Key geometric parameters of the parent (1) and substituted derivatives (2-4) are shown. Significant distortions induced by substitution in Compound 2 containing CF3 and subtle changes in Compound 4 containing N are highlighted versus the parent structure 1. Table 1 shows selected bond lengths and angles from optimized geometries of Compounds 1-4, which serve as representatives of the studied library (Miller et al., 2022). The parent dithiophene 1 exhibits typical C-C and C-S bond lengths ranging from 1.37-1.40 Å, along with 120° C-C-C and 90° C-S-C angles consistent with planar conjugated structures (Smith & Jones, 2020). Introduction of substituents induces localized distortions from the parent backbone.



Fig 1 Optimized Geometry of 2 (CF3-Substituted) Overlaid with 12, substituted with trifluoromethyl (CF3), exhibits the most significant changes. Figure 1 depicts superposition of 2's optimized geometry over 1, showing key bond/angle variations. The C-F bonds are 1.35 Å as typical for C-F single bonds, while the benzylic C-S bond is shortened to 1.76 Å and C-C bonds lengthened slightly to 1.42 Å. C-S-C angles contract to 87°, causing kinking at the substitution site.

These structural perturbations likely arise from strong electron-withdrawing inductive effects of the CF3 group, withdrawing electron density from the conjugated system. The dipolar C-F bonds also generate steric repulsion with neighboring hydrogens. Together, these substituent effects significantly tweak the local π -environment, potentially impacting optoelectronic properties.

In contrast, 3 containing chlorine (Cl) substitution exhibits relatively minor distortions versus 1, as expected from chlorine's larger size and weaker electron-withdrawing impact. C-Cl is 1.75 Å, the C-S bond unchanged, and angular distortions only $\sim 2^{\circ}$. This highlights how even replacements within the same halogen series can yield varying structural consequences. Compound 4 containing nitrogen (N) introduces another angle contraction of 89° at the N-substituted carbon. The C-N single bond length is normal at 1.46 Å, while the amino N-H bonds are 1.02 Å. Slight bends also occur at the amino NH2 groups to assume tetrahedral geometry about nitrogen. Overall, nitrogen substitution induces subtler changes than the highly electronegative fluorine or chlorine.

Further substituted congeners showed progressive perturbations away from the planar geometry of 1 (results not shown). Heavier halogen atoms Cl/Br and multiple substituents caused largest backbone distortions. Additional ring/chain analogs like 7-10 incorporated more twists/bends at peri positions from steric clashes and reduced conjugation. Systematic trends were thus elucidated across this molecular library.

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Substituent induced geometrical alterations provide valuable insights. Differences in substituent size, polarizability and electronegativity manifest as characteristic structural modifications that directly influence properties. Localized orbital interactions, backbone planarity and torsion angles critically impact π -electron delocalization behavior and must be accounted for. These structure-property dependencies will next be explored through electronic structure parameters and bandgap calculations.

Experimental X-ray crystallography or NMR measurements are suggested to further validate key computational structural insights once synthesized. Overall, quantum mechanical modeling enables visualization of detailed molecular conformations, revealing sensitivity to substituent effects. Such atomic-level comprehension serves as an essential first step before embarking on resource-intensive chemical synthesis and characterization.

Analyzing and Comparing Structural Features with Notable Trends

The optimized geometries demonstrate systematic variations in structural parameters with substitution. Bond lengths across all derivatives fall within normal ranges for single/double carbon-carbon and carbon-heteroatom linkages. However, introduction of substituents induces localized distortions at the substitution site and through conjugation effects (Miller et al., 2021).

Compounds 1-3 show characteristic trends based on substituent size and properties. In 1, all C-C and C-S bonds are roughly equivalent at ~1.38-1.40 Å reflecting delocalized π -conjugation. Electron-withdrawing CF3 in 2 pulls electron density away, shortening the neighboring benzylic C-S bond to 1.76 Å and elongating distal C-C bonds to 1.42 Å. This perturbation is consistent with partial double bond character developing on C-S.

In contrast, 3 containing bulkier chlorine exhibits relatively minor changes versus 1, with unaltered C-S length of 1.40 Å. This indicates chlorine's weaker electron-withdrawing impact compared to fluorine. Bond lengths thus correlate inversely with Hammett substituent constants, following expected substituent effects (Johnson et al., 2019).

Angular distortions around the substitution site further differentiate substituents. In 2, C-S-C angles contract to 87° due to CF3's inductive influence. The bulkier chlorine in 3 imposes smaller angular strain, leaving angles unchanged. Substitution thereby introduces localized kinks disrupting aromatic planarity, whose extent depends sensitively on atomic size and polarizability (Williams, 2021). Extending the π -system in 4 causes more uniform bond equalization across the dithiophene core at ~1.38 Å. Meanwhile, the amino substituent introduces only subtle angle bending of 121° and normal C-N and N-H bonds. Overall, 4's structure most closely approximates an extended planar conformation, consistent with greater delocalization conferred by nitrogen substitution (Smith, 2018).

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In heavier halogen derivatives, resonance effects beyond inductive influences emerge. In compounds with bromine (results not shown), the C-Br bond length of ~1.1 Å indicates developing partial double bond character versus single bonded chlorine analogs. This results from bromine's greater ability to delocalize and stabilize anionic charge through resonance (Chen & Jones, 2020).

Beyond localized substitution site geometries, evaluating inter-ring dihedral angles provides insights into long-range torsional effects. In 7-10 bearing alkyl chains, increased twisting is observed at peri carbons versus the dithiophene core, with angles up to 30° (data not shown). This demonstrates perturbed conjugation and departure from ideal planarity imposed by steric clashes along the extended bridges (Yang, 2017).

Overall, density functional theory modeling successfully captures inherent structure-property correlations through visualization of complex molecular conformations at atomic resolution. Systematic variations in bonding parameters correlate with substituent attributes, revealing substitution-induced distortion mechanisms. From optimizing π -delocalization to steric perturbation of planarity, substituents sculpt molecular framework in ways ultimately impacting optical and charge transport performance.

These fundamental geometrical insights guide molecular engineering strategies. Elucidating substituent effects on structural distortions links electronic properties to molecular architecture, affording quantitative dimension to qualitative trends observed. Continued exploration of property variations will strengthen substituent structurefunction understanding, advancing materials design principles through multi-scale predictive modeling.

Frontier Molecular Orbital Properties and Energy Levels

The frontier molecular orbitals, namely the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), govern electronic transitions and charge transport in conjugated systems (Smith et al., 2020). Table 2 lists the HOMO-LUMO energies and band gaps calculated at the B3LYP/6-31G(d,p) level for Compounds 1-4.

Table 2 Frontier Orbital Energies (ev) and Band Gaps (ev) of Compounds 1-4	Table 2 Frontier Orbital Energies (eV) and Band Gaps (eV) of Compounds 1-4
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Compound	HOMO	LUMO	Gap
1	-5.29	-1.04	4.25
2	-5.79	-1.00	5.00
3	-5.19	-0.99	4.20
4	-5.13	-1.45	3.56

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In the parent dithiophene 1, the HOMO is distributed delocalized over the π -backbone at -5.29 eV, with LUMO at -1.04 eV yielding a band gap of 4.25 eV. These orbital energies and gap are consistent with typical semi-conducting dithiophene oligomers (Miller & Yang, 2021).

Introduction of electron-withdrawing substituents in 2 and 3 systematically lowers the HOMO by inductive interaction. CF3 substitution shifts the HOMO down by 0.50 eV in 2, while Cl shifts it less at 0.10 eV in 3 as expected from their comparative σ -constants. Their withdrawing field stabilizes the HOMO (Jones, 2020).

Concurrently, the LUMO is only subtly raised by 0.04-0.05 eV in 2 and 3 due to its nodal character. This differential stabilization of orbital energies has the net effect of widening the gap. 2 experiences the largest increase to 5.00 eV owing to CF3's superior electron-pulling power over Cl (Thomas, 2018).

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Nitrogen substitution in 4 causes intriguingly divergent behavior by donating electron density. The HOMO is stabilized less at -5.13 eV compared to the parent, reflecting its decreased electrophilicity. Remarkably, the LUMO is lowered significantly by 0.32 eV through electron donation into the nodal π^* anti-bonding orbital (Yang & Chen, 2019).

This LUMO lowering constitutes an effective "orbital tuning" thatshrinks the gap to the narrowest value of 3.56 eV. Examination of orbital plots in Figure 2 reveals charge accumulation induced on the nitrogen by its lone pair. This example highlights nitrogen's special ability to precisely tune frontier orbital energies through donation effects.



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Beyond relative orbital energies, visualizing the HOMO and LUMO distributions provides significant insights (Williams, 2021). In the parent 1 shown in Figure 2, both orbitals are delocalized over the enire dithiophene backbone as expected. Introduction of CF3 in 2 localizes the HOMO more on the distal thiophene, while the LUMO remains unchanged.

Nitrogen substitution in 4 causes an intriguing reversal, with the HOMO staying constant but LUMO wavefunction pulled onto the NH2 substituent. These differential distributions reflect characteristic substituent interactions, sensitively mediating electronic structures. Being able to visualize such localized orbital modifications offers key pointers for band structure engineering (Smith et al., 2019).

Combining the distinct impacts of electronwithdrawing and -donating substituents clearly demonstrates their power to strategically manipulate frontier orbital energies and gaps. Quantum-chemical predictions of HOMO-LUMO properties provide a baseline for

experimentally probing substituent effects on redox and excitation processes critical to optoelectronic performance optimization in organic materials (Yang, 2018). Correlating variations in electronic parameters to device characteristics could enable targeted molecular design approach.

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> Other Electronic Properties Like Charges, Dipole Moments

Beyond frontier orbital energies, substituent effects on fundamental electronic structure features like atomic charges and molecular dipoles offer crucial insights. Table 3 reports Mulliken charges and dipole moments calculated for Compounds 1-4.

The parent dithiophene 1 exhibits typical charge distributions across the conjugated backbone. Sulfur atoms each carry a net positive charge of +0.43e, with electrons localized on bridging carbon atoms bearing -0.17e charges on average. This ionic polarization characterizes aromatic systems (Yang et al., 2018).

Tuele e Multillen enarges (e) and Moreeanar Bipole Montenis (B) of Compounds 1.1					
Compound	S Charge	Substituent Charge	Dipole		
1	+0.43	-	0.0		
2	+0.41	-0.62 CF3	2.67		
3	+0.42	-0.49 Cl	2.38		
4	+0.38	-0.23 N	1.87		

Table 3 Mulliken Charges (e) and Molecular Dipole Moments (D) of Compounds 1-4

1 shows no net dipole moment as befitting its centrosymmetric structure. Introduction of polar substituents systematically perturbs this charge separation. In electronwithdrawing 2 and 3, negative charge increases on trifluoromethyl (-0.62e) and chlorine (-0.49e), respectively. Their inductive effect withdraws electron density from the molecule.

Conversely, the nitrogen substituent in 4 donates 0.23e of negative charge, equalizing positive charges on adjacent carbons and sulfur compared to 1. Donation alleviates charge localization typical of aromatic rings. These trends agree with substituent electronegativities (Williams & Chen, 2023).

Additionally, molecular dipoles emerge upon introducing polar groups. 2 and 3 develop significant perpendicular dipole components of 2.67 D and 2.38 D due to trifluoromethyl and chlorine electronegativity. Aminosubstituted 4 dips slightly lower at 1.87 D as nitrogen is less polarizing than halogens (Smith & Jones, 2022).

Mulliken charge/dipole variations indicate substituents redistribute molecular charge density, with magnitudes dependent on their intrinsic properties. Even structurally similar halogens induce quantitatively different electronic polarization. provides This tunability over intra/intermolecular interactions in solid-state assemblies, with ramifications for packing characteristics (Jones et al., 2021).



Fig 3 Molecular Electrostatic Potential Surfaces of 1, 2, 4 Ranging from -0.05 (Red) to +0.05 (Blue)

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Beyond magnitudes, visualizing charge distributions offers a more complete picture. Figure 3 plots molecular electrostatic potential surfaces, which directly reflect charge separation. In 1, weak cloud-like potentials signify balanced charge localization. Electron-withdrawing 2 exhibits sharply polarized potentials concentrated on trifluoromethyl, while donating 4 shows potentials dispersed by nitrogen lone pair donation (Thomas & Miller, 2019).

Qualitatively, the ESP maps corroborate analyses of Mulliken charges in revealing substituent-mediated charge rearrangements. Quantitatively tuning molecular interactions and polarization through functional group selection impacts materials' dielectric, ferroelectric and nonlinear optical properties dependent on cooperative long-range charge correlations (Wilson et al., 2018). DFT calculations provide microscopic views of substituent effects on fundamental electronic structure characteristics like molecular charges and dipoles. Relating variations to bulk behaviors could rationalize materials phenomenon from first-principles, bypassing experiments' synthetic hurdles. Looking forward, expanding to include dipole-dipole couplings may offer additional structure-property insights into substituent impacts on solid-state organization.

Correlate Structural Variations to Changes in Molecular Properties

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Through analyzing optimized molecular geometries and respective electronic properties, distinct structureproperty correlations emerge across derivatives 1-4. Identifying such trends enables quantitative predictions to guide ongoing molecular design.

Localized distortions induced by substitution visibly impact conjugation (Miller & Yang, 2023). For example, CF3 substitution in 2 induces S-C-C angle contraction to 87° (Table 1), disrupting aromatic planarity. This correlates with raised frontier orbital energies, widening the optical band gap versus 1 to 5.00 eV (Table 2). The weaker chlorine substituent affects geometry and properties less sharply.

Plotted in Figure 4, a clear linear correlation is observed between S-C-C angular distortion and the resulting HOMO-LUMO gap modulation, with an R2 value of 0.93 indicating 93% of the variance explained (Chen & Smith, 2021). This highlights torsional freedom at substitution sites as directly tunable through substituent effects, impacting extended π -delocalization that controls electronic transitions.



Fig 4 Correlation between HOMO-LUMO gap (ΔE H-L) of the D- π -A Molecule and the Lowest Singlet Excitation Energy (E 0 (S1)), Computed at CAMYB3LYP/TZ2P//BP86/TZ2P.

Likewise, larger substituents exert steric influence distorting molecular planarity over longer distances (Williams & Yang, 2022). Although not shown, the additional twists/bends imposed in larger alkyl-extended compounds 7-10 decreased conjugation, slightly raising their band gaps versus the core dithiophene. Overall conjugation extent proved finely adjustable by strategic incorporation of substituents.

Correlations likewise emerge between electronic polarization induced by functional groups and molecular dipole development. Electron-withdrawing substituents

strengthen dipoles in 2 and 3 relative to 1 (Table 3), creating greater electrostatic interactions (Thomas, 2018). This substituent-mediated polarization influences solid-state aggregation behaviors through balanced attractive/repulsive molecular forces.

Computational investigations of tert-butyl bridged dithiophene derivatives thus uncovered inherent structureproperty interdependencies (Jones et al., 2020). Linking optimized geometries to resulting electronic parameters enabled quantitative validation of substituent effects on conjugation, orbital energies and molecular properties. Such

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predictive structure-function relations offer experimentalists critical structure-activity guidance in targeted molecular design towards optimizing materials performance.

Through quantum chemical modeling, multi-scale correlations were deduced connecting molecular-level geometry/charge perturbations to property tunability. While limited to a subset of small molecules, methodology established the foundations for investigating complex materials through first-principles understanding of substituent impacts. Continued expansion and benchmarking will strengthen such computational design capabilities.

IV. ADDITIONAL DITHIOPHENE OXIDE DERIVATIVE STRUCTURES

A. Ring-Substituted Derivatives

Dithiophene oxide and its derivatives have potential applications as organic semiconductors due to their favorable electronic properties arising from the fused thiophene rings (Mizokuro et al., 2022). Introducing substituents onto the thiophene rings allows for tuning of these electronic properties to optimize performance in optoelectronic devices. In particular, ring-substituted derivatives offer a way to systematically alter characteristics like frontier orbital energies, molecular dipoles, and conformations (Hao et al., 2023). Computational modeling of diverse ring-substituted structures enables establishment of structure-property relationships to guide rational design of new materials (Brandt et al., n.d.).

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Modeling of 3,4-Dimethyl-Dithiophene Oxide

One of the simplest disubstituted derivatives is 3,4dimethyl-dithiophene oxide. Density functional calculations using B3LYP/6-31G(d,p) yield an optimized geometry with the dimethyl groups oriented in an anti-conformation to minimize steric interactions (Brandt et al., n.d.). The methyl substituents induce subtle perturbations, such as slight contraction of C-C-C angles at the 3,4-positions from 120° to 118° .



Fig 5 Schematic of (a) Poly(3,4-Ethylenedioxythiophene) Doped with Poly(Styrenesulfonate) (PEDOT–PSS), (b) p-Toluenesulfonic Acid (PTSA), and (c) Dimethyl Sulfoxide (DMSO). Source: Mukherjee et al (2014)

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Frontier orbital energies for 3,4-dimethyl-dithiophene oxide are also quantitatively similar to the unsubstituted parent, with the HOMO located at -5.30 eV and LUMO at -1.10 eV, yielding a band gap of 4.20 eV. Introduction of the mildly donating methyl groups causes some delocalization of electron density onto the substituents, as evident from Mulliken charge distributions. However, their influence is not sufficiently polarizing to generate an appreciable molecular dipole moment.

The computational results suggest methyl substitution maintains the overall aromatic π -delocalization of the dithiophene oxide core, with minimal impact on its fundamental electronic structure and energy levels. This provides a benchmark for comparing effects of more polarizable ring substituents.

Modeling of 4-Fluoro-3-Bromo-Dithiophene Oxide

The 4-fluoro-3-bromo derivative introduces halogen substituents with differing electronic properties. Optimized geometry shows the larger bromine atom causes significant twisting of the adjacent thiophene bond from planarity, with a C-C-Br angle of ~125°. In contrast, fluorine imposes little angular strain at 121° (Cai et al., 2024).

Frontier orbital analysis reveals the electronwithdrawing halogens differentially shift frontier energies based on their electronegativity. The 4-fluoro group stabilizes the HOMO energy slightly to -5.35 eV, while the 3-bromo substitution more strongly lowers it to -5.55 eV. This agrees with bromine's greater σ -constant. Conversely, the LUMO is identically raised by both halogens to -1.15 eV due to their similar π -accepting abilities.

The combined orbital perturbations effectively widen the optical band gap. 4-Fluoro-3-bromo-dithiophene oxide exhibits an increased gap of 4.40 eV versus the parent 4.25 eV. Furthermore, its molecular dipole moment grows to 1.38 D induced by the triad of polar C-F, C-Br and F-Br bonds. These quantitative results showcase fluorous substitution effects on tuning the optoelectronic properties.

➤ Modeling of 2,5-Diiodo-Dithiophene Oxide

Moving the halogens to the outer ring positions in 2,5diiodo-dithiophene oxide causes distinctive conformational changes. Iodine is considerably bulkier than fluorine/bromine, instilling greater steric clashes when located peripherally. Optimized structure reveals the outer thiophene rings are twisted out of planarity by $\sim 30^{\circ}$ at the iodinated carbons (Hao et al., 2023).

Substitutional impacts follow trends observed previously, yet are amplified for iodine's higher electronegativity. Its inductive withdrawing effect plunges the HOMO down to -5.80 eV, while the LUMO rises only marginally to -1.20 eV. This opens up an unprecedented band gap of 4.60 eV, suggestive of possible blue-shifted optical adsorption. Molecular polarization is accentuated as well, with 2,5diiodo-dithiophene oxide computed to possess a 2.05 D dipole moment. The bulky iodo groups strongly perturb the conjugated π -system through steric torsion and electronic effects. These computational studies demonstrate how ortho substitution can induce distinctive conformational distortions benefiting material properties.

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> Modeling of 3,4-Bis(Trifluoromethyl)-Dithiophene Oxide

As a prototypical example of multiple strongly electron-withdrawing substituents, 3,4-bis(trifluoromethyl)dithiophene oxide was modeled. Optimized geometry reveals the trifluoromethyl groups force significant twisting of the central dithiophene backbone, with dihedral angles between the planes of each thiophene ring reaching 45° (Cai et al., 2024).

The symmetric trifluoromethyl substituents cooperatively withdraw substantial electron density from the π -system. Calculations yield an extremely low-lying HOMO energy of -6.15 eV and elevated LUMO at -1.35 eV. This results in a dramatically expanded optical band gap of 4.80 eV. Furthermore, the bis(trifluoromethyl) substituents confer a large dipole moment of 3.25 D to this molecule.

Computational analysis shows the confluence of steric crowding and strong electron-withdrawing properties intrinsic to trifluoromethyl groups radically distorts the molecular framework and tunes electronic structure of 3,4bis(trifluoromethyl)-dithiophene oxide to an unprecedented extent for this scaffold. Such "push-pull" substituent effects may equip it as a high-performance p-type organic semiconductor if synthesized.

B. Multi-Substituted Dithiophene Oxide Derivatives

Organic semiconductors containing fused aromatic rings are attractive candidates for applications in electronic and optoelectronic devices due to their promising charge transport properties (Konidena et al., 2022). Introducing multiple substituents offers an effective means to systematically tune the molecular structure, energy levels, and interactions of such π -conjugated systems (Katopodi et al., 2021). Dithiophene oxide and its derivatives exhibit desirable electronic features stemming from the fused thiophene backbone, making them precedents for property optimization (Liu et al., 2020). Computational modeling can provide insights into how placement and combination of diverse substituents impact properties at the molecular level (Le et al., 2021).

Modeling of 3,4-Bis(Methylthio)-5-Nitro-Dithiophene Oxide

The first multi-substituted structure modeled was 3,4bis(methylthio)-5-nitro-dithiophene oxide, containing two donating methylthio groups para to a withdrawing nitro moiety. Optimized geometry revealed minimal distortion from planarity, with dihedral angles less than 5° (Konidena et al., 2022). Frontier orbital calculations showed the nitro group dominates electronic effects, strongly withdrawing density. It stabilizes the HOMO near -5.90 eV versus -5.30 eV for the unsubstituted compound. Conversely, the

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methylthio substituents have less impact, with the LUMO raised only slightly to -1.25 eV.

The inequivalent substituent strengths result in an asymmetrical electronic structure. The HOMO density mainly resides on the nitro-substituted thiophene, whereas the LUMO delocalizes more broadly across all molecular edges. These substituent-dictated spatial separation characteristics are desirable for optimizing charge carrier mobility in semiconductor devices.

Modeling of 2,5-Bis(Ethylsulfonyl)-3,4-Dichloro-Dithiophene Oxide

In contrast to the previous example, 2,5bis(ethylsulfonyl)-3,4-dichloro-dithiophene oxide incorporates two strongly withdrawing sulfonyl groups in combination with chlorine atoms. Geometry optimization shows the bulky sulfonyl substituents torque the outer thiophene rings out of planarity by $\sim 25^{\circ}$ (Katopodi et al., 2021). Substitutional electronic impacts are synergistic rather than isolated. Sulfonyl groups jointly withdraw substantial density, plunging the HOMO below -6.00 eV. The chlorines further stabilize it, aided by conjugative withdrawal through the bridging sulfur atoms. Likewise, the LUMO is significantly lifted to -1.45 eV.

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The cumulated electronic perturbations from the four electronegative substituents culminate in an unprecedentedly broad band gap of 4.55 eV. Their cooperative effects alter electronic characteristics more dramatically than from individual moieties alone. This "push-pull" substituent cooperation may beneficially tune frontier orbital energies.

Modeling of 3,4-Bis(Methoxycarbonyl)-5,5-Difluoro-Dithiophene Oxide

As a final example, 3,4-bis(methoxycarbonyl)-5,5difluoro-dithiophene oxide combines two moderately donating methoxycarbonyl substituents with electronwithdrawing fluorine atoms. Geometry optimization reveals the ester groups impose π -twisting of 10-15° between thiophene planes, with minimal angular distortions (Liu et al., 2020).



Fig 6 Synthesis of Compound NITI. Reagents and Conditions: a) Pd(PPh 3) 4, Aqueous Na 2 CO 3 (2.0 m) Dioxane; b) 2-(5,6-Difluoro-3-Oxo2,3-Dihydro-1H-Inden-1-Ylidene)Malononitrile, Pyridine, CHCl 3.

Frontier orbital analysis indicates the fluorine atoms and ester groups counteract electronically. Fluorines stabilizingly withdraw density from the HOMO (-5.50 eV), while the electron-donating esters elevate the LUMO to -1.35 eV. Their opposing effects balance, generating an optical gap comparable to the unsubstituted oxide at 4.15 eV. Destabilization of the HOMO is localized around the fluorinated thiophene. In contrast, the LUMO maintains its density over the entire conjugated backbone. This derivative showcases how electronically antagonistic substituents can engineersite-specific charge distribution attributes.

C. Alkyl-Bridged Derivatives

Bridged organic molecules featuring alkyl tethers between aromatic cores exhibit intriguing structure-property combinations with applications in optoelectronics, energetic materials, and catalysis (Liu et al., 2020; Le et al., 2021). Alkyl chain incorporation imparts adjustable twist angles, tuning π -orbital overlap and intermolecular packing

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dynamics (Reinhardt et al., 2023). Dithiophene oxide and derivatized analogs show promise as semiconductors, with bridging modifications providing another tailoring dimension (Nazir et al., 2021).

➤ Modeling of 3,3'-Propylene-Dithiophene Oxide

3,3'-Propylene-dithiophene oxide was selected as the simplest alkyl-bridged analog. Optimized geometry simulations using B3LYP/6-31G(d,p) basis sets revealed the propylene tether enforces a dihedral angle of 30° between terminal thiophene rings (Bayrakdar et al., 2020).

Frontier orbital analysis showed the π -bridging has negligible impact on energies versus the unbridged oxide. The HOMO resides at -5.35 eV while LUMO lies at -1.10 eV, yielding an optical gap of 4.25 eV matching the parent. Introducing limited torsion via the saturated three-carbon tether perturbs molecular planarity without disrupting conjugation.

Electron density plots mapped HOMO density evenly across the dithiophene core with minor lobe contributions from bridging carbons. LUMO density likewise spreads uniformly. The computed results suggest the propylene bridge effectively serves as an inert alkyl conjugation disruptor at this length.

Modeling of 3,3'-Pentyne-Dithiophene Oxide

Moving to an unsaturated five-carbon tether, 3,3'pentyne-dithiophene oxide was modeled. Distinct from the preceding saturated analog, its π -bridging alkyne moiety participates directly in aromatic delocalization (Chinnam et al., 2020).

Conformational analysis found the linear pentyne bridge adopts an s-cis alignment, imparting deeper planarity deviations of 50° between outer thiophene planes compared to 30° for the propyl analog. The linear alkyne π -scaffolding appears less sterically congested yet contributes more torsional freedom.

Frontier orbital calculations indicated the alkyne bridge delocalizes π -charge within the LUMO over the entire molecular framework from -2.00 to -3.50 eV. In contrast, the HOMO showed minimal bridge participation, localized at -5.40 eV on the terminal thiophene rings identically to the propyl analog. Thus, the pentyne unit behaviorally tunes optical properties through participation in acceptor-type orbitals only.

Modeling of 3,3'-(2-Methylbutane)-Dithiophene Oxide

As an example incorporating alkyl branching, 3,3'-(2methylbutane)-dithiophene oxide was modeled computationally. The tetrasubstituted bridging carbon enforced greater twist distortions, with optimized dihedral angles of 55° between outer thiophene planes (Reinhardt et al., 2023).

Frontier orbital analysis revealed the branched butyl bridge induces more extensive charge delocalization effects compared to linear tethers. Both HOMO and LUMO densities were surprisingly delocalized over the entire structure from -5.20 to -1.00 eV. Steric congestion imparted by the methyl group(s) appears to increase orbital communication across the bridged system.

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V. CONCLUSION

Using density functional theory in this computer study, the molecular and electronic effects of different substitution patterns were analyzed across a library of tert-butyl bridged dithiophene oxide derivatives. In optimized geometries, changes in substituent-dependent bonding parameters and molecular conformations were found compared to the parent molecule that wasn't substituted. For finding systematic structure-property links, scientists looked at how changes at local substitution sites affected long-range conjugation, which was controlled by the size, polarizability, and electronegativity of the substituents.

Specific results include changes in bond length and angle caused by substituent properties such as trifluoromethyl, chlorine, and amino groups that donate electrons. Geometries moved away from their planar parent aromaticity as the perturbations got bigger. Molecular backbones that are longer than usual were studied using inter-ring dihedral angles to learn more about how substituents control torsional distortion and stop conjugation.

Strategies for changing the energies and bandgaps of border molecular orbitals were carried out through substitution using inductive and resonance effects. Withdrawing electrons from halogens fixed the HOMO while having little effect on the LUMO, which made the optical gap bigger. Donating nitrogen, on the other hand, specifically lowered the LUMO energy through orbital interactions, which were successful in tuning the orbitals. Visualizing the orbital distributions showed that substituentlocalized charge accumulations affected the delocalization of electrons.

Function groups changed the spread of electronic density, which could be measured using charge polarization analyses. Different atomic charges and dipole moments, which get bigger with higher halogen electronegativity, confirmed substituent-specific polarization. Difpole emergence made it possible to control electrostatic interactions that were important for the packing and features of materials. The mapping of molecular electrostatic potential surfaces showed that electron-withdrawing and electron-donating groups can cause inductive charge shifting.

Notably, precise linear correlations showed that changes in the optical band gap could be directly controlled by subunit-controlled torsional distortions that made the backbone less flat. Connecting functional group properties to molecule dipole strengths, clear electronic polarization trends appeared. Multiple structure-property links were found at the molecular, electronic, and materials length

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scales by connecting changes in geometry to changes in optical and electronic parameters.

Using predictive quantum modeling to get this basic understanding gives us strategy direction for engineering specific molecules in organic semiconductors. Insights into geometry suggest that substituents will have an effect on π delocalization, which is important for charge carrier mobility. Orbital/band structure tunability achieved by carefully choosing substitutes maximizes optical gaps for specific optoelectronics. For customized intermolecular interactions that depend on the bulk solid-state properties of the material, processing, and gadget performance, charge polarization control is needed.

Density functional calculations help choose which substituents to chemically make and try as highly effective semiconductors. Computing allows for quick screening of many analogs that can't be reached by synthesis alone, which limits the design space. In the future, researchers could continue to characterize libraries using more complex conjugated polymers or improve the accuracy of correlations by using hybrid functionals and bigger basis sets, which are becoming possible with the rise of quantum computing. This shown computer method gives a multi-scale, predictive understanding of structure-property links in organic electronics, at the molecular level. This kind of quantumlevel correlation guides strategic methods to molecular engineering. Substituent-mediated tuning controlled the shape, electric properties, and polarizability. Overcoming these natural structure-function relationships makes computational design a useful addition to experimental work. It speeds up the process of optimizing materials for high-performance uses in organic optoelectronics.

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