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CONFORMATIONAL ANALYSIS OF A FURAN, THIOPHENE ALTERNATING π SYSTEM

by

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A thesis submitted to the faculty at The University of Mississippi in partial fulfillment of the requirements of the Sally McDonnell Barksdale Honors College

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Abstract

Organic materials with conjugated π-electron networks are increasingly being studied as an alternative to inorganic semiconductors. In order to effectively transport charge as a semiconductor, the organic materials should maintain a planar conformation, exhibit π conjugation, and be rigid to rotational interconversion. Both furan and thiophene systems have been investigated as potential organic semiconductors but difficulties with solubility, synthesis, and effectiveness hampered these efforts. A novel furan-thiophene hybrid system that exhibits promising semiconducting properties is examined here. Full geometry optimizations and corresponding harmonic vibrational frequency computations were run on a diverse set of potential furan and thiophene oligomer structures using the GAUSSIAN09 software package. Scans of the potential energy surface were also computed in order to determine the rigidity of the system. All computations were done at the B3LYP/6-31G(d,p) level of theory. Overall, it was determined that the hybrid systems consisting of alternating furan and thiophene rings stemming from a central benzothiadiazole (BTD) ring have promising structural properties. The most promising structures were ones with low relative energies, high rotational barriers, and planar conformations. The lowest energy structures are those in which the furan rings are directly connected to the central BTD ring and adopt an anti polarity to the furan O atom away from the S atom in BTD. As subsequent rings are added to the system, the rotational barrier is largely unchanged, with little preference to the conformation of these additional rings.
1. Introduction

1.1 Organic Materials with Conjugated π-electron Networks

Organic materials with conjugated π-electron networks are increasing in popularity due to their potential application in optoelectronic devices. They are cost effective, naturally abundant, versatile, and relatively easy to synthesize. Therefore, organic conjugated materials are being developed as alternatives to inorganic semiconductors.\textsuperscript{1,2} Potential applications for organic electronics include organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), organic photovoltaics (OPVs), solar cells, and biochemical sensors.\textsuperscript{1} Conjugation, the overlap of p-orbitals in series separated by σ-bonds, is important for these polymers because it provides a network of electron delocalization, thus increasing their semiconducting capabilities.\textsuperscript{2} To be effective chemically, the organic materials must be rigid to rotational interconversion and have tight solid state packing.\textsuperscript{1,3} Ideally, semiconducting molecules should exhibit π conjugation and maintain a planar conformation in order to effectively transport charge.\textsuperscript{3} However, synthesizing these materials in a controlled manner can be extremely challenging.
1.1.1 Thiophene

Oligothiophenes are naturally found in the roots of *Asteraceous* plants and appear to be a potential material for synthesis of optoelectronic devices.\(^4\) However, thiophenes, Figure 1, pose a variety of challenges to both the synthesis and electronic performance of the oligomer.\(^5\) They have low solubility in organic solvents, requiring the use of additional solubilizing groups during synthesis. Their electronic properties, specifically luminescence, are decent but far from efficient. Additional structures, such as electron acceptors, are required to increase the electronic efficiency of these systems.\(^6\) Given the synthetic challenges and low luminescent capabilities, this system is far from ideal when designing optoelectronic devices.

![Figure 1. A: Single thiophene molecule. B: Thiophene oligomer.](image)

1.1.2 Furan

Initially, oligofurans, Figure 2, were rarely used due to their difficult synthesis, crystallization, and instability under oxidative conditions.\(^1,7\) After successful creation, they were found to have a variety of desirable properties. In comparison to oligothiophenes, oligofurans showed increased tight solid-state packing and lower reorganization energy, meaning they exhibit increased charge delocalization and rigidity upon hole transfer.\(^1\) The hole mobility, a measure of the degree to which the charge carrying hole can be transferred, and therefore a measure of the semiconducting potential, was found to be 1.6 times higher for a furan system than an equivalent thiophene system.\(^7\)
Additionally, they are naturally found as terpenes in both marine and terrestrial organisms and have been utilized in synthetic reactions.\textsuperscript{4,7}

\begin{center}
\begin{tabular}{cc}
A & B \\
\end{tabular}
\end{center}

Figure 2. A: Single furan molecule. B: Furan oligomer.

1.1.3 Thiophene-Furan Hybrid

Investigating hybrid furan-thiophene systems is particularly interesting because of the potential improvements in optoelectronic properties such as stacking distance, solubility, and charge transport. Varying the identity and conformation of the heteroatoms present on the sidechain heterocycles can drastically alter the electronic, optical and physical properties of the molecule.\textsuperscript{2,8} A previous study investigated the impact of altering the ratio of thiophene to furan rings on the electronic properties of the system, but few have studied their corresponding conformation.\textsuperscript{8} A series of experiments have been conducted on a fused thiophene furan hybrid system, Figure 3. The results showed that placing the furan rings towards the interior, Figure 3a, resulted in a more planar structure and an increase in fluorescent electronic properties than when the thiophenes were placed towards the interior, Figure 3b.\textsuperscript{8} Another study investigated mixed linear (non-fused) thiophene-furan systems of varying lengths (up to three rings), Figure 4.\textsuperscript{9} They reported, using the Hartree Fock/6-31G(d,p) level of theory, that the rotational barrier remains constant as the length of the chain increases.\textsuperscript{9} They also studied the rotational barrier for two linear thiophene rings and a hybrid thiophene-furan
system. They reported a barrier of 1.04 kcal mol$^{-1}$ and 3.05 kcal mol$^{-1}$ for the thiophene system and hybrid system respectively.$^9$

![Figure 3](image1.png)

Figure 3. Structures of fused thiophene-furan hybrid oligomers. A: Structure with furan on the interior. B: Structure with thiophene on the interior.

![Figure 4](image2.png)

Figure 4. Linear, non-fused furan-thiophene hybrid structure.

### 1.1.4 BTD

Benzothiadiazole (BTD), Figure 5, has recently proved to be a successful electron-accepting core, which can potentially increase desirable optoelectronic properties.$^3$ Given its ambipolarity, it is a promising central structure in which thiophene and furan rings can be added to increase its effectiveness as both an electron and hole transporter.

![Figure 5](image3.png)

Figure 5. Benzothiadiazole structure.
1.1.5 Furan-Thiophene Hybrid with BTD

This study investigates an alternating (non-fused) system of furan and thiophene rings originating from a central BTD ring, Figure 6, but one might expect results similar to the studies mentioned earlier (without BTD). The main goal of this project will therefore focus on the consequences of varying the identity and directionality of the heteroatom, with respect to the thiadiazole on the central BTD ring. Switching from an all thiophene to an alternating hybrid system decreases intersystem crossing and thus improves electronic properties due to oxygen having smaller spin-orbit coupling than sulfur. Oxygen also has a smaller atomic radius than sulfur, thus adding furan to the system leads to a more tightly-packed, dense backbone relative to the all thiophene system. Consequently, this decreases the intermolecular spacing, resulting in a more electronically efficient system. Further, the presence of the furan rings improves the solubility of the system and decreases the need for solubilizing groups. Combining those properties with the electron-accepting BTD core could lead to a more efficient optoelectronic device.

Figure 6. Example structure of an alternating, furan-thiophene hybrid oligomer with a central BTD ring.
1.2 Computational Chemistry

Simulation is an extremely valuable tool in a variety of fields. From the healthcare field to the classroom, modeling helps to predict potential negative and positive outcomes without actually performing the desired action. In the field of chemistry, modeling serves as an extremely important purpose. It allows, for example, one to compute molecular properties on systems that are difficult or dangerous to synthesize. This saves time and resources, allowing a computational chemist to study the fundamental properties of a system and giving a synthetic chemist knowledge of the most effective molecule.

Computational chemistry is the branch of science that allows one to investigate chemical problems on a computer. Such chemical problems that can be examined include molecular geometries, chemical reactivities, and molecular and transition state energies among many others. In order to effectively study these topics, computational chemists utilize a variety of methods, or a combination of them, including: molecular mechanics, molecular dynamics, semiempirical, density functional theory, and ab initio. Each method has its own advantages and disadvantages. However, all of them have been used to simulate the behavior of physical atoms and molecules. Classical physics is at the core of molecular mechanics. Applying quantum mechanics to chemistry results in quantum chemistry methods, which include semiempirical, density functional, and ab initio approaches.

Quantum is defined as a discrete quantity, and mechanics is defined as studying the behavior of a system under a force. Together, quantum chemistry means studying the behavior of electrons under the electromagnetic forces present in atoms and molecules.
subject to the laws of quantum mechanics. This is the definition of quantum electronic structure theory but many refer to this as quantum chemistry. The use of quantum mechanics in chemistry has its roots in the early 1900s. Historically, quantum mechanics came about due to a lack of agreement between the theory of classical physics and atomic level experiments. The discontinuity between theory and experiment led to the development of quantum mechanics, largely driven by two novel ideas: quantization and wave-particle duality.

1.2.1 Quantization

One of the major disagreements between theory and experiment was evident upon measuring the spectral density of blackbody radiation. Classical physics predicted that as frequency increases, the spectral density will increase to infinity, as shown in Figure 7.

![Figure 7. Spectral density of blackbody radiation for both the classically predicted model and Planck's revised model at a variety of temperatures.](image-url)
This means that at all temperatures above zero, there will be an infinite amount of energy emitted from a blackbody, known as the ultra violet catastrophe because classical theory was incorrect at high frequencies. Experimental curves agree with classical theory at low frequencies, but as the frequencies increase, the spectral density reaches a maximum value and then decreases. To solve this conundrum, Max Planck derived a new equation (1) that depended on frequency. Planck’s goal was to match experiment with theory, and the only way to achieve this was to assume that frequency was continuous and energy was quantized, meaning it has discrete values.

\[ E = n \hbar \nu \] (1)

Using equation 1, Plank then revised the formula for spectral density to be equation (2)

\[ \rho(\nu, T) d\nu = \frac{8\pi \hbar^2 \nu^3}{c^3} \frac{1}{e^{\hbar \nu / k_B T} - 1} d\nu \] (2)

Although Plank’s ideas were initially disregarded because people did not agree with the discrete nature of energy, Einstein’s work with the photoelectric effect later validated Plank’s assumptions.

**1.2.2 Wave Particle Duality**

Classical physics predicted that when light interacts with a metal surface, it acts as a wave over the entire surface. Therefore, all of the electrons on the surface will absorb a small portion of light and electrons will be emitted from the surface as long as the intensity is sufficiently high. Additionally, intensity was thought to be a function of each electron’s kinetic energy. However, the photoelectric effect proved that when light of a certain wavelength is incident on a metal surface, an electron will only be ejected if the
energy of the light is greater than the potential for the metal surface. Einstein concluded that the energy of light is related to its frequency, not intensity, shown in equation (3).

\[ E = h\nu \]  

(3)

Each electron’s kinetic energy is related to the frequency of the light, but the number of electrons emitted is dependent on the intensity of the light. Even at low intensities, electrons can be emitted from a metal surface because light energy can be concentrated on a single electron, proving the particle nature of light.

Further, the double slit diffraction experiment shows that light can behave as both the classically modeled wave and newly found particle.\(^1\) During this experiment, light is incident on a single slit followed by a double slit. Because of the nature of the diffraction patterns, light is thought to behave as a wave, but when the light is observed at individual time periods, it behaves as particles. Classical theory attempts to classify light as either a wave or a particle whereas quantum mechanics states that light can exhibit both wave and particle behavior.

1.2.3 Electronic Structure Theory

Electronic structure theory describes how electrons move in atoms or molecules, usually under the assumptions of the Born-Oppenheimer approximation, which is discussed later.\(^2\) Because electrons are on such a small scale, quantum mechanics is needed in order to properly describe the nature of the electrons in a system.\(^2\) Quantum mechanical theory suggests that electrons cannot be localized and should therefore be thought of in a wave-like state.\(^2\) Wavefunctions are used to determine the probability of
finding an electron at a certain location and these wavefunctions can be solved for using the Schrödinger equation.\(^\text{12}\)

### 1.2.4 Schrödinger Equation

The Schrödinger equation is used to describe the wave-like nature of matter. It comes about by combining the classical wave equation with the de Broglie equation, giving equation (4).

\[
-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)
\]

(4)

This is the 1D time-independent Schrödinger equation which can be applied to three dimensions, shown in equation (5).

\[
-\frac{\hbar^2}{2m} \left( \frac{\partial^2\psi(x)}{\partial x^2} + \frac{\partial^2\psi(y)}{\partial y^2} + \frac{\partial^2\psi(z)}{\partial z^2} \right) + V(x, y, z)\psi(x, y, z) = E\psi(x, y, z)
\]

(5)

This is the 3D time-independent Schrödinger equation which allows one to compute the total energy of the system. When the Hamiltonian operator, shown in equation (6), acts on a wavefunction, the result is said to be an eigenfunction if the result is the original function multiplied by a factor, the eigenvalue. Using the Hamiltonian to operate on the wave function will therefore give the total energy of the system multiplied by the wave function.

\[
\hat{H}\psi = E\psi(x) \quad \text{where} \; \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \hat{V}
\]

(6)

For certain systems, wave functions can be obtained when the boundary conditions are known. This computed energy is critical when comparing isomers and allows for the prediction of molecular properties associated with the system. However, the Schrödinger
The Schrödinger equation cannot be analytically solved for multi-electron systems just like any 3 body system in classical physics. The Hamiltonian, total energy operator, shows why the Schrödinger equation cannot be solved for molecules. At the most basic level, a molecule has two types of energy: kinetic energy and potential energy. This energy can come from both the nucleus and the electrons in the molecule. Therefore, the Hamiltonian can be written as shown in equation (7) with \( n, e, T, \) and \( V \) signifying nucleus, electron, kinetic energy, and potential energy respectively.

\[
\hat{H}_{\text{electronic}} = \hat{T}_n + \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee} \quad (7)
\]

The potential energy of the nucleus-electron interaction term is problematic because it prevents the separation of the total energy operator into isolated nuclear and electronic components.\(^\text{13}\) Therefore, the Born-Oppenheimer approximation is employed in order to better understand molecules. Because the nucleus has a much larger mass than the surrounding electrons, the nucleus is assumed to be fixed in comparison to the movement of the electrons.\(^\text{13}\) It is under this premise that approximations can be made. First, the kinetic energy term of the nucleus goes to zero since the nucleus is assumed to be non-moving.\(^\text{13}\) Similarly, the potential energy of the nucleus-nucleus interaction term is removed from the equation because it is constant. This means that equation (7) simplifies into equation (8).

\[
\hat{H}_{\text{electronic}} = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} \quad (8)
\]

In expanded form, equation (8) can be written as equation (9) where \( m_e, Z_j \) and \( r \) represent the mass of an electron, nuclear charge, and radius, respectively.
\[ \hat{H}_{\text{electronic}} = -\sum_{l}^{n} \frac{\hbar^2}{2m_e} (\nabla_{r_l}^2) - \sum_{j=0}^{N} \sum_{l\neq j}^{n} \frac{Z_j}{r_{lj}} + \sum_{l=0}^{n} \sum_{k\neq l}^{n} \frac{1}{r_{lk}} \]

Where \( \nabla_{r_l}^2 = \frac{\partial^2}{\partial x_l^2} + \frac{\partial^2}{\partial y_l^2} + \frac{\partial^2}{\partial z_l^2} \) \hspace{1cm} (9)

It is the very last term that is challenging to solve analytically and that is where computational programs are useful. They can approximate electron correlation and subsequently give insight into the electronic structure of a system.
2. Computational Methods

2.1 Level of Theory

There are various approximate numerical procedures that can be used to determine the electronic properties of a system. Basis sets are mathematical functions that attempt to approximate the molecular orbitals used in a system. These functions can be any mathematical function as long as they are easily manipulated and their linear combinations generate reasonable molecular orbitals. Both Slater and Gaussian functions are the most commonly used computationally. Slater functions approximate atomic wave functions well but are computationally demanding. They involve two-electron integrals on four nuclei. This is a challenging problem mathematically but utilizing the Gaussian Product Theorem and linearly combining Gaussian functions aids in solving the problem. The Gaussian Product Theorem states that the product of two Gaussians is a third Gaussian. This means that using Gaussian functions reduces the number of two electron integral centers from four to two. However, these functions do not accurately describe the shape of the system as well as Slater functions. Therefore, one can linearly combine many Gaussians together in order to give these orbitals a more accurate shape without increasing the computational demand associated with adding more functions.

While the number of Gaussian functions that can be used for a system is infinite, there is a minimum number of functions needed to describe all the electrons. These are
referred to as minimal basis sets, but they are not used very often because they have too few functions for an accurate description. To overcome these shortcomings of the minimal basis set, split valence basis sets can be used. Split-valence basis sets have two different sets of functions: one set for the core orbitals and another for valance orbitals. For example, the 6-31G basis set represents the core orbitals of atoms like C,N,O, and F with six Gaussian functions and the valance orbitals with a set of three Gaussian functions and one Gaussian function.

There are a variety of methods that one can choose from when studying a system. Some of these methods are systematic and extremely accurate. Others are computationally demanding and therefore cannot be used for large systems. Therefore, a compromise must be made in order to obtain a general understanding of the system without sacrificing computational demand. The best approximation of an analytic solution to the Schrödinger equation uses a method that accounts for all electron correlation and uses a large basis set. Hartree-Fock uses a self-consistent field to treat each electron’s interaction with the average field of the other electrons in the system. This method is variational and size consistent but can often over-estimate the energy of the electron-electron repulsion. Configuration interaction methods such as CIS or CISD use single or double electron promotion to approximate and limit the number of electron excitation states on the basis of number of electrons. This method is variational but not size consistent. CISD is calculated from first principles, therefore it is classified as an \textit{ab initio} method. \textit{Ab initio} methods, such as second order Møller-Plesset perturbation theory, are size consistent. However, these methods are not variational, meaning that the solution for energy might be lower than the true value. All of the methods mentioned
thus far assume that electrons are motion correlated, a whole molecule can be calculated based on the electronic properties of atoms, and excited states can be systematically added into the system. Density functional methods however, take a different approach to describing a system. They make a generalized guess about how the electrons will interact with one another based on the behavior of an ideal system in the gas phase. Density functional methods use the electron density to solve for the system, which uses fewer variables than the typical wavefunctions.

This investigation will employ a density functional method, specifically B3LYP. B3LYP is a hybrid functional that uses both Hartree Fock exchange and density functional exchange-correlation. Becke’s 3-parameter exchange functional and Lee-Yang-Parr’s 3-parameter correlation functional are combined in this method. B3LYP was chosen due to its ability to adequately describe the system and accurately predict the general trends of related systems. The basis set being used for this study is 6-31G(d,p). This is a split valance double zeta basis set with $d$ polarization functions for heavy atoms such as C,N, and O, and $p$ polarization functions for hydrogen.

### 2.2 BTD Ring Structure

This study investigates the energetics of a large, highly conjugated molecule, therefore structural syntax is needed in order to understand the different structures. The central ring is benzothiadiazole (BTD), a conjugated system of benzene fused to a thiadiazole (TD), as shown in Figure 8.
Figure 8. Example structure from the 0+1 set of atoms. The name for molecule A is H_BTD_f, meaning that there is a H connected to C5 and a furan ring connected at C2, anti with respect to the S atom in BTD (for example, the 1-2-7-8 torsional angle θ1=180°). The name for molecule B is H_BTD_F, meaning that there is a H connected to C5 and a furan ring connected at C2, eclipsed with respect to the S atom in BTD (for example, the 1-2-7-8 torsional angle θ1=0°).

Furan, a five membered ring with oxygen, and thiophene, a five membered ring with sulfur, are added systematically in chains from the central BTD ring at carbons 2 and 5, shown in Figure 8. When no rings are added to carbon 5 on BTD, a hydrogen atom exists there. There is a torsional angle, denoted as θ1, from carbon 1-2-7-8 (heteroatom). When the rings are coplanar with BTD, θ1=0° or 180°, and any angle between that means the rings must break planarity in order to achieve the lowest energy conformation.

Additional five membered rings will always be added from the carbon adjacent to the heteroatom (carbon 9), as shown in Figure 9. This means there will be additional torsional angles between the heteroatoms of adjacent rings (for example, the 8-9-12-13 torsional angle in Figure 9). Again, these torsional angles are related to the planarity of the system.
Figure 9. Example structure from the 0+2 set of atoms. The name for molecule A is H_BTD_Tt, meaning that there is a H connected to C5, a thiophene ring attached to BTD at C2 with $\theta_1$ near 0° and a second thiophene attached to the first at C9 with an alternating pattern (for example, the 8-9-12-13 torsional angle $\theta_2= 180^\circ$). The name for molecule B is H_BTD_TT, meaning that there is a H connected to C5, a thiophene ring attached to BTD at C2 with $\theta_1$ near 0° and a second thiophene attached to the first at C9 with a similar conformation (for example, the 8-9-12-13 torsional angle $\theta_2= 0^\circ$).

Structures are labeled with letters to represent the linear order of rings. Furan rings are denoted with the letter “f” or “F” and thiophene rings are denoted with the letter “t” or “T”. When the innermost ring has the eclipsed conformation with BTD ($\theta_1=0^\circ$), the ring is denoted with a capital letter. When the innermost ring has the anti conformation with respect to BTD ($\theta_1=180^\circ$), the ring is denoted with a lower case letter. For example, the image in Figure 8 would be named H_BTD_f because there is a hydrogen connected to BTD on the left hand side while a furan ring is attached to the other side with a torsional angle, $\theta_1=180^\circ$.

Similarly, as more furans or thiophenes are connected to the oligomer, the same structural syntax exists. If the heteroatom on the outer five membered ring is eclipsed with respect to TD, the outer ring is given an uppercase letter. If the heteroatom on the outer five membered ring is anti with respect to TD, the outer ring is given a lower case letter. For another example, the image in Figure 9 would have the name H_BTD_Tt. A hydrogen is connected to the left of BTD while and two thiophene rings are attached to
the other side, with the innermost ring being eclipsed with respect to TD (θ1=0°) and the outermost ring being anti with respect to TD (θ1=180°).

To summarize, all rings are denoted by the first letter of the name of the ring. Further, the capitalization of the letter is determined by the ring’s conformation with respect to TD.

2.3 Potential Energy Scans

Potential energy surfaces can be calculated to depict the relative energies along a reaction coordinate. The simplest potential energy surface to imagine is one with a diatomic molecule. The bond length will start infinitesimally small and gradually increase in length. As the bond length changes, the energy of the molecule will change as well. When the molecules are too close together, shown at the far left asymptote in Figure 10, the energy increases to infinity, is at a maximum, and represents a lack of bonding between the molecules. When the molecules are infinitely separated, shown at the far right asymptote in Figure 10, the energy increases before leveling off, remains constant, and the molecules are dissociated. Graphing this scan of the potential energy surface allows one to visualize the lowest energy structure for the molecule. Figure 10 shows the restricted potential energy surface for LiH as a reference. The graph shows that the energy of LiH is at a maximum when atoms are infinitely close, at a minimum at the equilibrium bond length (1.6 Å), and increases as the two atoms are separated to infinity. This potential energy surface is shown with experimental data fitted to a Morse potential, and is used here as a reference to compare the accuracy of the theoretical
potential energy surface. The B3LYP method was used with the 6-31G basis set, which appears to give a good approximation for the lowest energy structure.

![Potential Energy Surface LiH](image)

**Figure 10.** Potential Energy Scan for LiH showing both theoretical and experimental results.

The potential energy surfaces presented in this study are of a slightly different form than the one presented above. For this study, it isn’t the bond length that is allowed to increase, but instead it is a torsional angle associated with the heteroatoms on the outermost ring and its inner neighboring ring. The torsional angle from atom 1-2-7-8 in Figure 8 (θ1), or the torsional angle from atom 8-9-12-13 in Figure 9 (θ2), is allowed to rotate 180° in 15° increments with all other geometrical parameters being optimized. The energy is then computed at each increment and used to construct a potential energy curve. Computationally, this is accomplished via a feature in Gaussian09\textsuperscript{19}, specifying which atoms are to rotate and by how many degrees each time. Figure 11 is shown here as an example potential energy curve. The x-axis shows the value of the torsional angle of 0° representing the eclipsed conformation and 180° representing the anti-conformation. The y-axis shows the relative energy of each conformation in kcal mol\textsuperscript{-1}. As the torsional
angle increases to $90^\circ$, the energy of the system increases, suggesting an energetic barrier exists upon modification of the torsional angle. Once the transition state (TS) conformation is reached, the relative energies decrease as the torsional angle approaches $180^\circ$. Once the two furan rings are anti from each other, they are in their lowest energy conformation.

![Figure 11. Sample potential energy surface for a 0+2 molecule.](image)

### 2.4 Symmetry

Potential energy scans are useful to depict a $180^\circ$ rotation of the outermost torsional angle starting from a planar structure. However, when the lowest energy structure is non-planar for systems containing two or more rings on the same side of BTD, a $180^\circ$ scan will not provide a complete picture of the torsional profile. To account for this lack of symmetry, a full $360^\circ$ scan was performed on these systems. Due to the
lack of planarity in the lowest energy structure of systems H_BTD_tt, H_BTD_Tt, H_BTD_Ff, and H_BTD_Ft, two scans were conducted. Figure 12 shows an example of the two potential energy scans.

Figure 12. Full 360° rotational scan for the H_BTD_tt system because it is non-planar.

This figure shows that a full 360° scan is needed in order to visualize the full rotational profile. The scan reveals a rotational barrier of about 3.39 kcal mol\(^{-1}\) relative to the lowest energy conformation near \(θ_2≈180°\).

### 2.5 Transition State Optimizations

The rotational barrier was determined by taking the difference in energy from the transition state (highest energy) and the minima (lowest energy). Transition states cannot be physically observed but they are imaginary structures that occur during the course of a reaction. Computationally, they are visualized on the potential energy surface as a maximum energy peak that can achieve a lower energy state by moving one step
downhill in either direction. Transition states for rotations were located as well as the minima points for each conformation. Computationally, this was achieved by using the “opt(TS)” keyword, which looks for a structure in the uphill direction. Harmonic vibrational frequency computations were performed to verify that the lowest energy conformation was a minimum and the highest energy conformation was a transition state. Minima on the potential energy surface should have no imaginary frequencies whereas transition states should have exactly one imaginary frequency. This was verified for all of the structures studied. The consistency of the rotational barrier was measured by comparing the full potential energy scan and the transition state search through Gaussian09. Because finding the transition state structure is computationally demanding, once the rotational barrier was verified for the 0+1 and 0+2 sets, transition state searches were no longer carried out. Therefore, all rotational barriers will be reported as the difference in energy from the highest point to the lowest point on the potential energy surface.
3. Results and Discussion

Results will be presented in order of increasing complexity of the system, with the goal of identifying the lowest energy, planar conformation and characterizing the corresponding rotational barrier.

3.1 Systems with One Ring (0+1)

The first set of systems studied is referred to as 0+1 because there is one heteroatom ring attached to BTD and a hydrogen atom on the other side, shown in Figure 8. There are two different systems in this set: one with a furan ring and the other with a thiophene ring. For each of these systems, two quasi-planar conformations were identified. Comparing the two systems, furan has a much larger barrier to rotation (8.01 kcal mol⁻¹) than thiophene (4.58 kcal mol⁻¹), shown in Figure 13. Therefore, attaching furan to BTD instead of thiophene will lead to a larger rotational barrier and a more rigid backbone for larger systems. Comparing the energies for the different conformations of the furan system, furan would much rather have a torsional angle of θ₁=180° (BTD_f) than θ₁=0° (BTD_F). This BTD_f conformation is preferred by 4.09 kcal mol⁻¹. The previously defined torsional angle for this system is exactly 180°, indicating that this system is planar (C₃ symmetry). However, the optimized BTD_F is not planar and has a θ₁ torsional angle of 23°. This same result holds true when comparing the two
conformations of the thiophene system, although the energy difference is much smaller. The optimized structure of BTD\_t is perfectly planar and lower in energy by 0.82 kcal mol\(^{-1}\) than BTD\_T. When the eclipsed BTD\_T conformer is optimized it breaks planarity and adopts a \(\theta_1\) torsional angle of 16.7°. The energy difference for all optimized structures is presented in Table 1.

![Potential energy scans](image)

**Figure 13.** 0+1 Potential energy scans. \(\theta_1=0^\circ\) corresponds to the heteroatom being eclipsed to the S atom of BTD. \(\theta_1=180^\circ\) corresponds to the heteroatom being anti with respect to the S atom on BTD.

**Table 1.** Relative energies (in kcal mol\(^{-1}\)), torsional angles (\(\theta_1\) in \(^\circ\)), and rotational barriers (in kcal mol\(^{-1}\)) for the optimized minima of BTD with one furan or one thiophene ring.

<table>
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<th></th>
<th>Rel. E</th>
<th>(\theta_1)</th>
<th>Barrier</th>
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<td>H_BTD_T</td>
<td>0.82</td>
<td>16.7</td>
<td></td>
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</table>
3.2 Systems with Two Rings (0+2)

The next system is referred to as 0+2 because there is a hydrogen atom on one side of the BTD ring and two five membered rings on the other side of BTD. There are more systems in this set than the 0+1 due to the additional complexity. There can be two furans, with a variety of different conformations, or two thiophenes, with a variety of different conformations. Additionally, there can be one thiophene and one furan, with two possibilities for their connectivity to the BTD ring and many different conformations. Following the results of the 0+1 data, the inner ring should prefer to be anti ($\theta_1=180^\circ$) with respect to the S on BTD.

Starting with the system of two furans, the inner ring does prefer to be anti ($\theta_1=180^\circ$) with respect to S on BTD by at least 3.87 kcal mol$^{-1}$. Allowing the inner ring to be eclipsed with respect to BTD ($\theta_1=13.4^\circ$) forces the outer ring to break planarity with the inner ring by $\theta_2=1.5^\circ$. Further, the outer ring prefers to have the reverse conformation ($\theta_2=180^\circ$) relative to the inner ring (BTD_fF), this conformation being 1.53 kcal mol$^{-1}$ lower in energy than having both furans in the same conformation with a torsional angle of $\theta_2=0^\circ$ (BTD_ff).

Similarly, in a system with two thiophene rings, the inner ring prefers to be anti ($\theta_1=175.4^\circ$) with respect to S on BTD by at least 0.79 kcal mol$^{-1}$, just as the 0+1 results suggest. However, this system must break planarity by at least $\theta_2=15.2^\circ$ in order to have two adjacent thiophenes. Like the all-furan system, the outer thiophene ring prefers to have the reverse conformation to the inner thiophene ($\theta_1=164.1^\circ$) (BTD_tT) by 0.71 kcal mol$^{-1}$. 


When the system is composed of one thiophene and one furan, the lowest energy conformation is one in which the inner ring is anti with respect to the S on BTD ($\theta_1=180^\circ$). This conformation is consistent with the 0+1 results and is energetically favorable by at least 3.81 kcal mol$^{-1}$. Additionally, the hybrid system with furan adjacent to the BTD ring is 4.34 kcal mol$^{-1}$ lower in energy than the conformation with thiophene adjacent to BTD. When furan is the innermost ring, the thiophene outer ring has little preference for the direction it is facing; the lowest energy conformation consists of the inner furan ring with a torsional angle of $\theta_1=180^\circ$ and the outer thiophene with a torsional angle of $\theta_2=0^\circ$, but this is merely 0.08 kcal mol$^{-1}$ lower in energy than when the outer thiophene has a torsional angle of $\theta_2=180^\circ$. This means the two structures have similar energetics. Therefore the results of the 0+2 data, Table 2, show that the hybrid with the inner furan ring anti to TD is the lowest energy conformation regardless of the directionality of the outer thiophene.

Regarding the rotational barrier, Figure 14, as the system increases in number of ring additions, the goal is that the rotational barrier will remain reasonably high (~5 kcal mol$^{-1}$); indicating the presence of a rigid backbone that is important synthetically. The rotational barrier associated with the second thiophene ring is lower by 1.19 kcal mol$^{-1}$. Similarly, the rotational barrier for the second furan ring is lower by 1.87 kcal mol$^{-1}$. The system with two thiophenes has the smallest rotational barrier at 3.39 kcal mol$^{-1}$, showing its low rigidity. The system with two furans has a rotational barrier of 6.14 kcal mol$^{-1}$, showing it has a slightly more rigid backbone. The furan-thiophene hybrid was expected to have a rotational barrier somewhere in between the energies of the two furan and two thiophene systems. As expected, the rotational barrier of the hybrid with inner thiophene
(BTD_tf) is 5.12 kcal mol\(^{-1}\) and the hybrid with inner furan (BTD_ft) is 4.92 kcal mol\(^{-1}\), showing the similar energetics at this level of theory. However since the inner furan system is 4.34 kcal mol\(^{-1}\) lower in energy than the inner thiophene, this substantial energy difference makes the inner furan system more desirable.

Figure 14. 0+2 Potential energy scans. \(\theta_2=0^\circ\) corresponds to the adjacent rings having the same conformation. \(\theta_2=180^\circ\) corresponds to the adjacent rings have reverse conformations.
Table 2. Relative energies (in kcal mol\(^{-1}\)), torsional angles (θ1 and θ2 in °), and rotational barriers (in kcal mol\(^{-1}\)) for the optimized minima of BTD with two rings.

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3.3 Systems with Three Rings (0+3)

The next system studied is referred to as 0+3 because there is a hydrogen on one side of BTD and three adjacent rings on the other side of BTD. Because the results of the 0+1 and 0+2 scans showed that the lowest energy conformation has the innermost ring anti to TD, only those systems were considered from this point forward.

In the all-furan system, the lowest energy conformation is one in which all rings have an alternating conformation with the innermost furan having a torsional angle of θ1=180° (BTD_fFf). All of the systems studied in this set are planar. For example,
BTD_fFF is planar with torsional angles of θ1=180°, θ2=180°, and θ3=0° and BTD_ffF is planar with torsional angles of θ1=180°, θ2=0°, and θ3=180°.

The all-thiophene system shows similar results with the BTD_tTt being the lowest in energy. However, all of the fully optimized thiophene systems break planarity (θ1≈177°, θ2≈20° or 170°, and θ3≈30° or 160°). As additional rings are added, the torsional angle gets further away from being planar with θ1, θ2, and θ3 puckering by about 3°, 10-20°, and 20-30° respectively.

The rotational barrier energy, as shown in Figure 15, for both the all thiophene and all furan systems remains high (~6 kcal mol⁻¹ for furan and ~3.30 kcal mol⁻¹ for thiophene) and similar to the 0+2 data. The rotational barrier for 0+3 thiophene is only 0.09 kcal mol⁻¹ smaller than the 0+2 results and the rotational barrier for 0+3 furan is only 0.12 kcal mol⁻¹ less than the 0+2 results. This suggests that adding more rings out does not substantially alter the rigidity of the backbone.
Figure 15. 0+3 Potential energy scans. $\theta_3=0^\circ$ corresponds to the adjacent rings having the same conformation. $\theta_3=180^\circ$ corresponds to the adjacent rings have reverse conformations.

As the 0+2 results predicted, the lowest energy conformation for the hybrid 0+3 system is one with furan on the innermost ring and thiophene in the middle (BTD_ftf). Changing the outermost rotational angle $\theta_3$ from $180^\circ$ (BTD_ftF) to $0^\circ$ (BTD_ftf) is only preferable to by 0.04 kcal mol$^{-1}$, making these systems isoenergetic at this level of theory. Additionally, the systems with the middle thiophene having a rotational angle $\theta_2=180^\circ$ are only 0.1 kcal mol$^{-1}$ higher in energy than the lowest energy conformation of $\theta_2=0^\circ$. Therefore, it’s reasonable to conclude that the hybrid system does not have a significant preference for a certain conformation in the second or third ring as long as the innermost ring is furan. All of these conformations are planar. Regarding the rotational barrier, the
innermost furan hybrid system has a rotational barrier of 4.96 kcal mol$^{-1}$ which is 0.04 kcal mol$^{-1}$ higher than the 0+2 hybrid.

Similarly, there is no clear lowest energy conformation in the thiophene hybrid system. The BTD$_{tfT}$ system is slightly preferred by 0.05 kcal mol$^{-1}$ over the BTD$_{tFt}$ system. When the innermost ring is thiophene, there is no significant energetic preference for the torsional angle to be $\theta_2=0^\circ$ or $\theta_2=180^\circ$. The rotational barrier for the thiophene hybrid system remains high at 4.95 kcal mol$^{-1}$, which is 0.17 kcal mol$^{-1}$ less than the comparable 0+2 hybrid.

Table 3. Relative energies (in kcal mol$^{-1}$), torsional angles ($\theta_1$, $\theta_2$, and $\theta_3$ in $^\circ$), and rotational barriers (in kcal mol$^{-1}$) for the optimized minima of BTD with three rings.

<table>
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<th>$\theta_3$</th>
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<td>180.0</td>
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</table>
3.4 Systems with One Ring on Each Side (1+1)

Increasing the complexity of the system, rings are added to both sides of the central BTD. This next set of systems is referred to as 1+1 because there is one ring on each side of the BTD. When one side has furan and the other has thiophene, both prefer to be anti with respect to the S on BTD (θ₁=180°) but furan has a much larger preference for this. Agreeing with the 0+1 results, having the thiophene ring with a torsional angle of 180° is 0.77 kcal mol⁻¹ lower in energy relative to the torsional angle of 0°. Similarly, having the furan ring with a torsional angle of 180° is 4.18 kcal mol⁻¹ lower in energy relative to when the torsional angle is 0°. Further, the rotational barrier is larger for furan (8.20 kcal mol⁻¹) compared to thiophene (4.74 kcal mol⁻¹), making the furan system preferable because it has a more rigid backbone, as seen in Figure 16. This data is comparable to the 0+1 data, Figure 16, for separate furan and thiophene systems, showing that these methods are generating consistent results.
Figure 16. 0+1 vs 1+1 Potential energy scan. θ₁=0° corresponds to the heteroatom being eclipsed with respect to the S on BTD. θ₁=180° corresponds to the heteroatom being anti with respect to the S on BTD.

Table 4. Relative energies (in kcal mol⁻¹) and torsional angles (θ₁ in °) for the optimized minima of BTD with one ring on either side.

<table>
<thead>
<tr>
<th></th>
<th>Rel. E</th>
<th>θ₁</th>
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<td>Scan Max (t)</td>
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<td>90.0</td>
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3.5 Systems with Two Rings on Each Side (2+2)

Further increasing the complexity of the systems, the next set is referred to as 2+2 because it has two rings on each side of BTD. There are many different possible systems for this set but only a select few were considered based on the results from the previous
sets. Restricting there to be an equal number of furans and thiophenes on each side, the lowest energy conformation has furans on the inner ring and thiophenes on the exterior, shown in Table 5. This lowest energy conformation has the inner rings anti with respect to the S on BTD (θ1=180°) and the outer rings with the same conformation, θ2=0°, (tf_BTD_ft). Forcing the thiophenes to have a torsional angle of θ2=180° increases the energy by 0.13 kcal mol\(^{-1}\), which at this level of theory exhibits essentially the same energy. Having the thiophenes as the inner rings and furans on the outside (ft_BTD_tf) increases the energy by 8.65 kcal mol\(^{-1}\), further indicating that furan should be the inner ring. Additionally, all of these conformations are planar.

As far as the rotational barrier is concerned, Figure 17, it requires 5.02 kcal mol\(^{-1}\) to flip the direction of the outer thiophene ring. As shown in Figure 17, this data is similar to the 0+2 and 0+3 rotational barrier for having an inner furan, meaning that increasing the number of rings coming off the BTD ring does not negatively impact the rigidity of the system.

When the earlier restriction is removed and two furans are allowed to be on one side with two thiophenes on the other side of the BTD ring, the energy increases by 7.29 kcal mol\(^{-1}\) compared to the lowest energy conformation. This conformation must also break planarity in order to occur, making it a non-ideal system.
Figure 17. 0+2 vs 2+2 Potential energy scan. θ2=0° corresponds to outer ring having the same conformation as the inner ring. θ2=180° corresponds to the outer ring having the reverse conformation compared to the inner ring.

Table 5. Relative energies (in kcal mol⁻¹), torsional angles (θ1 and θ2 in °, with left and right being used to illustrate the specific torsional angle as written in the first column), and rotational barriers (in kcal mol⁻¹) for the optimized minima of BTD with two rings on either side.

<table>
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<tr>
<th></th>
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<th>θ1(right)</th>
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3.7 Systems with Three Rings on Each Side (3+3)

Further increasing the complexity, the next systems studied are referred to as 3+3 because there are three heteroatom rings on both sides of BTD. Because the number of rings is increasing and the outermost ring is getting further away from the central BTD, the rotational barrier is most likely not affected by BTD, as shown in the 2+2 results. As the number of rings increases, the rotational barrier should primarily come from the energy barrier of rotating between the outer two rings. Therefore, the rotational barrier was computed for two adjacent rings, without the central BTD, as shown in Figure 18. Twisting a furan to be anti with respect to another furan requires 5.39 kcal mol\(^{-1}\) whereas twisting a thiophene to be anti with respect to another thiophene requires 2.74 kcal mol\(^{-1}\). Twisting a furan to be anti with respect to a thiophene requires 4.25 kcal mol\(^{-1}\) but there is no clear preference for the anti conformation.

Figure 18. Simple potential energy scan for two-ring, non BTD system. \(\theta=0^\circ\) corresponds to the conformation where the two rings are eclipsed. \(\theta=180^\circ\) corresponds to the conformation where the two rings are anti.
Based on these scan results, it was assumed that the rotational barrier should remain the same as adjacent rings are added to the system. This is consistent with the previously reported data that showed the rotational barrier was not substantially altered by adding additional rings. Therefore scans were no longer run for the 3+3 systems but one can hypothesize the trend would continue. Additionally, one would expect the lowest energy conformation to be the structure with furans directly connected to the central BTD on both sides in an anti conformation with respect to the S on BTD. Therefore, consistent with the previous results, the most optimal structure would be ftf_BTD_ftf with no conformational preference on the second and third rings.
4. Conclusions

Overall, the BTD system with alternating furan and thiophene rings appears to have promising synthetic properties. As the number of rings is increased from BTD, the rotational barrier remains high (~5 kcal mol$^{-1}$), ensuring that only one product is synthesized and not a mixture of two conformations. The most promising system has a planar structure, allowing for tight packing and good charge transport properties. Based on the data presented, the innermost ring connected to BTD should have an anti conformation with respect to the S on BTD. More specifically furan should be the innermost ring connected to BTD. It has the lowest energy conformation and a high rotational barrier (8.01 kcal mol$^{-1}$). As additional rings are added on to furan, the rotational barrier remains high (~5 kcal mol$^{-1}$), suggesting that the rigidity of the backbone is not substantially altered. Also, the alternating systems have little preference for the conformational direction of the second and third ring, as long as the inner furan ring is anti with respect to the S on BTD. However, as additional rings are added, there is a subtle preference for all of the rings to have the same conformation, $\theta_2=\theta_3=0^\circ$. To further study this claim with increasing accuracy, these molecules need to be studied at a higher level of theory. However, these results are in good agreement with previous experimental and theoretical results for similar systems.$^{8,9}$
References

 DOI: 10.1021/jp108125q

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