

Structural Insights for Molecular Design of Conjugated Molecule and Polymers

by

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Structural Insights for Molecular Design of Conjugated Molecule and Polymers

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Abstract

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Acknowledgments

Thank everyone here

Chapter 1

Introduction

Intro goes here

Chapter 2

Structural Changes in Doped and Excited Conjugated Polymers

2.1 Introduction

Conjugated polymers are promising materials for use in a range of applications such as light-emitting diodes, solar cells, battery materials, transistors, and actuators for artificial muscles.[76] These applications rely on the material being doped and or excited, where the resulting electronic conductivity and more specifically carrier mobility is governed by polymer chain structure.[61, 62] Although chain structure dictates carrier mobility, relatively little is known about the structure of doped or excited chains, especially at larger length scales ($\geq 5 \text{ nm}$). At smaller length scales ($< 5 \text{ nm}$) polarons and excitons are known to cause local structural distortions via electron-vibrational and electron-torsional coupling,[77, 89, 83, 11] but the collective impact on chain structure has not been quantified. Structural knowledge is fundamental to improving carrier mobility and other electronic properties in conjugated polymer materials.[6, 52]

In general, conjugated polymers at room temperature exhibit a mixture of semicrystalline and amorphous domains.[72] Emerging research have shown that connectivity between semicrystalline or disordered aggregate domains is critical, and surprisingly an increase in crystallinity does not equate to an increase in bulk carrier mobility.[75, 62] Instead, it is the specific material's ability to remain electronically connected while experiencing an inevitable amount of disorder that governs its conductivity,[62] as opposed to the intrinsic conductivity of a polymer chain. Both Son et al. and Noriega et al. provide schematics, on the domain level, to help visualize these concepts.[75, 62].

The ability of conjugated polymer materials to remain electronically connected depends on the structure of the amorphous chains that physically connect the semicrystalline or disordered aggregate domains.[62] Carrier mobility in amorphous regions is particularly sensitive to individual chain structure because chains regularly adopt non-planar conformations².[61] If a

²Although conformation and configuration are used somewhat interchangeably to describe polymer

chain torsion angle is in a sufficiently non-planar configuration², the conjugation pathway along the chain is disrupted, due to less p-orbital overlap, thus creating an energy barrier to transport that is insurmountable by carriers at room temperature. Disrupted conjugation essentially acts as a dead end,[75] similar to a kink in a garden hose blocking the flow of water. Aromatic conjugated polymers (e.g. polythiophene (PT), poly(3-hexylthiophene) (P3HT), polypyrrole (PPy), and poly(p-phenylene vinylene) (PPV)) are representative of chains that adopt non-planar torsional configurations in their ground state (undoped and unexcited) and will be the focus of this study. [25, 29, 49, 55] Furthermore, we place emphasis on polythiophenes because both PT and P3HT have recently been utilized in high mobility disordered polymers.[75, 87]

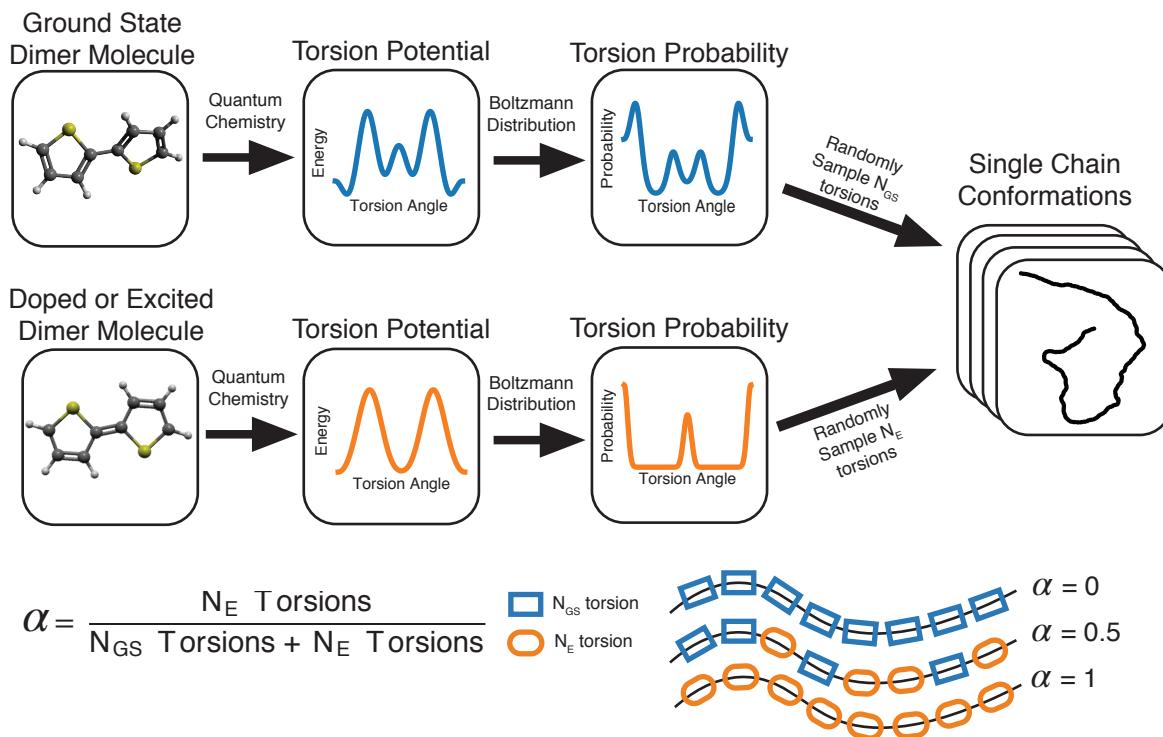


Figure 2.1: The torsion potential model algorithm for generating ensembles of single chain conformations. The variable α represents the fraction of doped or excited torsion angles along a chain.

A torsion-based approach to modeling doped and excited chains utilizes previous methods, and is physically motivated by the torsional nature of the doping and excitation process in aromatic conjugated polymers. Although amorphous polymers possess many structural degrees

structure, for the purposes of this article, a conformation refers to the structure of an entire chain, whereas a configuration refers to local structure within a chain (e.g. a torsional configuration).

of freedom, and statistical averages are necessary to describe the ensemble of conformations, the problem of modeling individual chains can be greatly simplified by allowing only the torsional degrees of freedom to fluctuate [28]. Taking this a step further, if neighboring torsion angles can be considered independent, individual chains are reduced to a set of uncorrelated torsion angles. This later assumption has been shown to be valid for semiflexible polymers such as PT and P3HT [81, 88]. As a result, chain models based on torsion potentials have been developed for aromatic conjugated polymers (e.g. PT and PPV),[88, 18] however, the effect of doping or excitation has not been considered.

In this article we determine the impact of torsional rearrangements, due to doping or excitation, on amorphous chain conformations and properties. Additionally, it is evident that these chains undergo fast and substantial nuclear relaxation upon doping or excitation,[89, 11] hence our objective is to study steady-state chain conformations and properties as a function of the doping or excitation level. A better understanding of these structural changes will provide insight for a variety of on-going and future strategies directed at tuning electronic conductivity of conjugated polymers.

2.2 Model

We developed a stochastic torsion potential model for generating chain conformations at various levels of doping and excitation, outlined in Fig. 2.1. A brief description of the model is provided here with more details in the Materials and Methods and Supplementary Information (SI). First, we calculate dimer ground, doped (cation), and excited (first triplet) state torsion potentials using quantum chemistry. Next, room temperature Boltzmann distributions are computed from associated torsion potentials. Finally, chain conformations are generated by randomly sampling the Boltzmann distributions based on the fraction of doped and excited torsion angles (α). After sampling an ensemble of chain conformations at each α value average chain properties such as persistence length, end-to-end distance, and planarity (S order parameter) can be calculated.

2.3 Results and Discussion

Torsion Potentials

When comparing torsion potentials from Fig. 2.2, the doped and excited potentials are qualitatively similar, yet very different from the ground state. Throughout the work presented here, the doped state refers to calculations preformed on a cation dimer, and the excited state refers to dimer calculations performed on the lowest energy excited state (i.e. the first triplet T1). While a direct photoexcitation to the lowest energy state (T1) is spin forbidden it is accessed via intersystem crossing,[7, 4, 50] and hence a good representation for steady-state behavior. In both the doped and excited potentials the number of minima and maxima are reduced, the location of the minima are shifted to planar configurations, and the relative

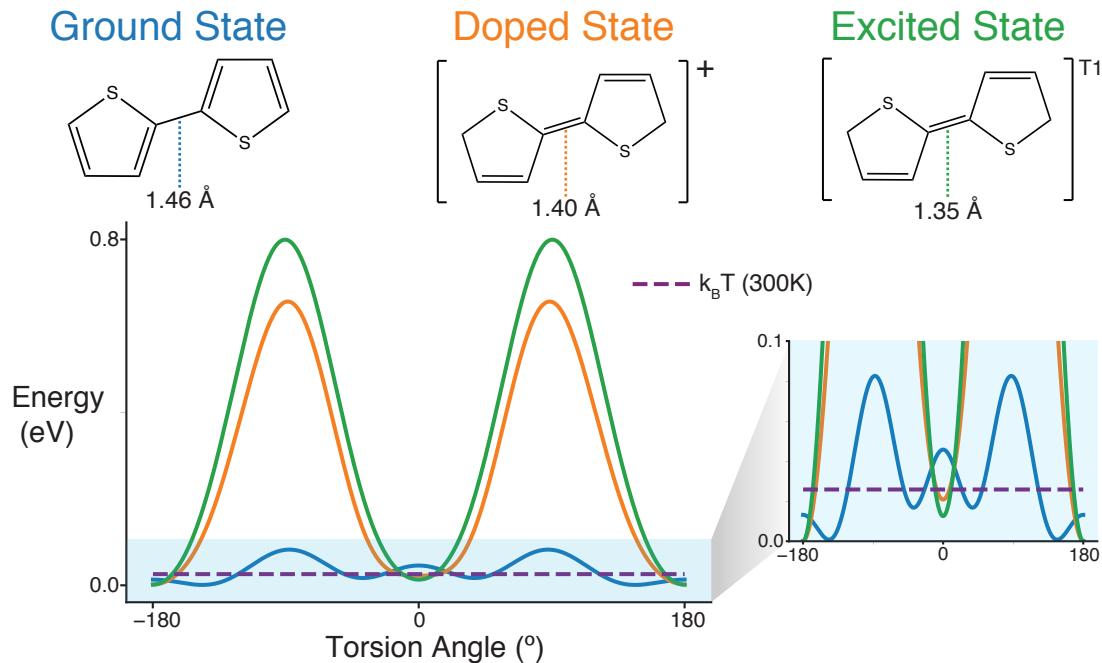


Figure 2.2: A comparison of torsion potentials, bridge bond lengths, and structures of the ground, doped (cation), and excited-state (triplet) thiophene dimer molecules. The doped and excited states are represented as quinoidal structures.

barriers between extrema are much higher. A similar trend can be seen for PPy in Fig. ???. The overall shape of the calculated torsion potentials is not sensitive to the level of theory or basis set used (see Fig. A.1), which suggests that the underlying physics are well captured. Nevertheless, we emphasize that the level of theory and basis set are important for capturing quantitative energy differences between configurations, especially for the cis (0° torsion angle) and trans (180° torsion angle) configurations in the doped and excited state.

The torsional differences between the doped and excited states and the ground state are due to an electronic structure rearrangement. Previous work has reported a transition from ground-state aromatic structure to quinoidal structure upon doping or excitation for a variety of conjugated polymers (aromatic and quinoidal PT structures are displayed at the top of Fig. 2.2).[68, 10, 80, 1, 4, 67, 11, 85, 29, 3, 8] Our results for PT and PPy (SI Section ??) support this conclusion. Doped and excited bridge C-C bond lengths were shorter as compared to that of the ground state (Fig. 2.2), signifying double bond character in the doped and excited states. Additionally, the doped and excited-state torsion potentials resemble that of ethylene, which has an ideal bridge C=C double bond.[70] Pronounced resonance (electron delocalization) is observed in both the doped and excited structures, such that the bridge C-C bonding character falls somewhere between a single and double bond. The excited state

exhibits more double bond character, based on the bridge bond length, which results in a steeper torsion potential as compared to that of the doped state.

A point of contention when determining polymer torsion potentials is the validity of a dimer to accurately represent the torsion potential of the larger chain. Indeed, earlier work on PT and P3HT suggest that longer chains are necessary for determining the torsion potential.[23] However, DuBay et. al. attributed the chain size effects to inadequate basis set size and relaxation procedure. Furthermore, DuBay et. al. demonstrated that dimers can accurately represent conjugated polymer torsion potentials when a sufficient level of theory, basis set, and relaxation procedure are used.[25] Our results, which examined ground-state (undoped and unexcited) chains up to 8 monomers, agree with DuBay et. al. in that chain length does not meaningfully impact the torsion potential of ground-state PT. While this conclusion does not hold *a priori* for doped or excited torsion potentials due to the additional complications of charge and spin localization, we nevertheless find that the doped dimer suitably characterize the torsion potential of the larger doped chain. SI Subsections A.1A.1 and A.1?? contain data and additional insight on the impact of the chain length on torsion potentials.

Persistence Length

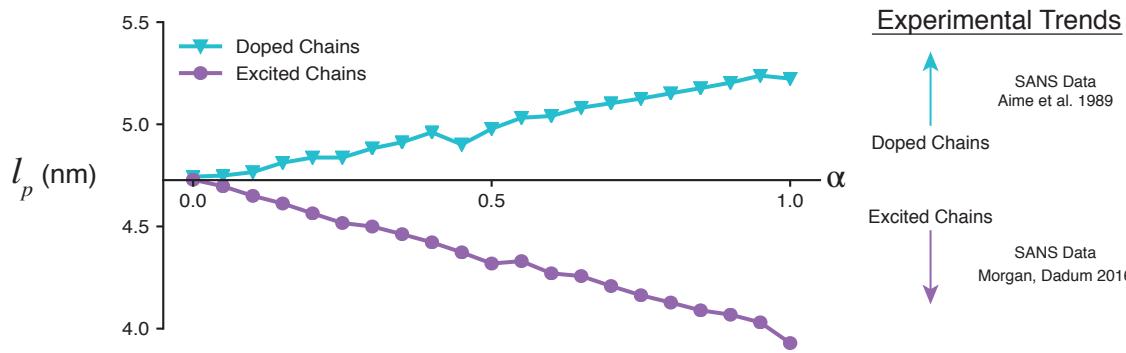


Figure 2.3: Left) Calculated persistence lengths (l_p) as a function of doping and excitation (α). Right) Experimental persistence length trends for doped and excited chains.

The trend in persistence length as a function of α (Fig. 2.3) highlights an important difference between doped and excited chains. Remarkably, the persistence length and the end-to-end distance of excited chains decrease with increasing α . We initially anticipated excited chains to be more linear as a result of the excited-state torsion potential. Indeed, the persistence length and end-to-end distance of doped chains increase with increasing α . In both types of chains the end-to-end distance can be related to the persistence length by the WLC model (eq. S??).

Comparing the calculated persistence length with experimental values reflect well on the obtained torsion potential model. The calculated ground-state PT persistence length of 4.7 nm, is in good agreement with a recently obtained experimental value of ~ 3 nm for P3HT[57] and a previous measurement of 5.5 nm for PT.[1] Moreover, McCulloch et al. observed the trend of decreasing persistence length with increasing side chain length, which indicates that PT should exhibit a persistence length longer than ~ 3 nm. In addition, the persistence length trend calculated for both doped and excited chains qualitatively agree with experimental observations.

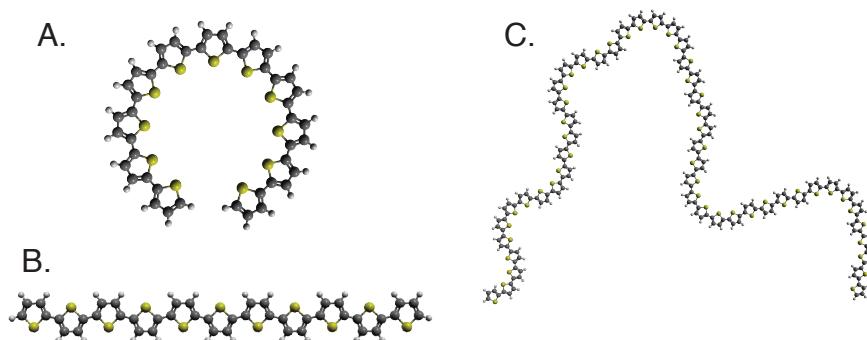


Figure 2.4: A) Circular all cis chain B) Linear all trans chain C) A random 1:1 mixture of cis and trans torsion angles. All conformations are completely planar.

The fraction of cis torsion angles in doped or excited PT chains dictates its persistence length and end-to-end distance. Figure 2.4 demonstrates the impact of cis torsion angles for an idealized case where $\alpha = 1$ and the torsion angle distribution is reduced to the two minima: 0° (cis) and 180° (trans). Figure 2.4A and 2.4B depict the circular cis chain and the linear trans chain respectively. The chain in Fig. 2.4C is a random 1:1 mix of cis and trans torsion angles, and clearly illustrates that a chain conformation can be completely planar yet highly non-linear. While the idealized case is an exaggeration of the real doped and excited chains, the histograms of the sampled torsion angles (Fig. ??-???) demonstrate that the primary difference between the doped and excited chains is the larger fraction of cis or close to cis torsion angles in the excited chains. This can be correlated to the smaller cis-trans energy gap in the excited torsion potential. The larger fraction of cis torsion angles in the excited chains cause them to become more non-linear than the doped chains, explaining the opposing trends in persistence length and end-to-end distance.

A small-angle neutron scattering (SANS) study of PT in solution also observed an increase in persistence length upon doping (Fig. 2.3).[1] An undoped PT persistence length of 5.5 nm was reported, in quantitative agreement with our calculated value of 4.7 nm. Aime et al. suggested that highly doped chains were rod-like, and attributed much of change in the persistence length to the “intrinsic rigidity” associated with a quinoidal electronic structure.

The magnitude of the persistence length increase was considerably larger than the results reported here, but torsional effects may only be partially responsible for the increase in persistence length. More importantly, the rod-like interpretation of the scattering results depends strongly on the scaling of the scattering vector (q), which was found to be $\sim q^{-1}$. Rod-like chains do scale as q^{-1} ,^[63] but a semiflexible 2D WLC can scale as $\sim q^{-4/3}$.^[17] The 2D WLC was not considered at the time, and the resolution of the scattering results may have been insufficient to differentiate between the two. Our results demonstrate the importance of considering chain planarity when interpreting scattering results of doped or excited conjugated polymers.

Another SANS study reported that upon excitation, P3HT chains decrease in length, in alignment with our findings (Fig. 2.3), although the reduction in persistence length reported (~ 3 nm) slightly exceeds our predictions from torsional effects alone (~ 1 nm at $\alpha = 1$).^[59] We speculate that other effects such as polymer-solvent interactions may contribute to the overall reduction in length. Additionally, we note that the reduction in chain length from beam damage was not completely clarified. Moreover, Morgan and Dadmun rejected polaron localization and chain planarization as it was assumed that these effects lead to more linear or longer chains, however as shown in this work, chain planarization does not necessarily lead to linear chains.

Planarity

Figure 2.5 shows the evolution of the order parameter S , which reduces planarity to a single scalar value with a clear physical interpretation. For instance, $S = 1$ represents a completely planar chain, whereas $S = 0$ represents an isotropic chain where rings exhibit equal probability of facing any direction. For comparison, typical ordered liquid crystals exhibit S values ranging from 0.3 - 0.8.^[19] S does not depend on the ordering of the torsion angles, which renders a more complicated polaron grouping unnecessary for determining S . As seen in Fig. 2.5, the parameter S monotonically increases with increasing α as expected based on the planar nature of the doped and excited torsion potentials. Although S was calculated for PT we expect the trend to be similar among other aromatic conjugated polymers because the electronic structure rearrangement that fundamentally determines the torsion potential of the doped and excited state is the same. Additionally, S depends on the length of the chain considered. Chain lengths were selected by experimental recommendations for optimum conductivity.^[62] However, if longer chains are of interest the S values reported here could be viewed as the planarity of a segment along the chain as no chain end effects were considered.

We expect a large increase in S to be associated with an increase in carrier mobility. Carrier mobility in conjugated polymers relies on a continuous conjugation pathway along the polymer backbone.^[73] As mentioned, the conjugation pathway can be disrupted if the rings along the chain are sufficiently non-planar. As a result, a conjugation length can be defined. The order parameter S is intimately related to the conjugation length as both are a measure of planarity, however S is a global measure whereas the conjugation length represents a local feature. Conjugation length is not reported here because it requires explicit treatment of

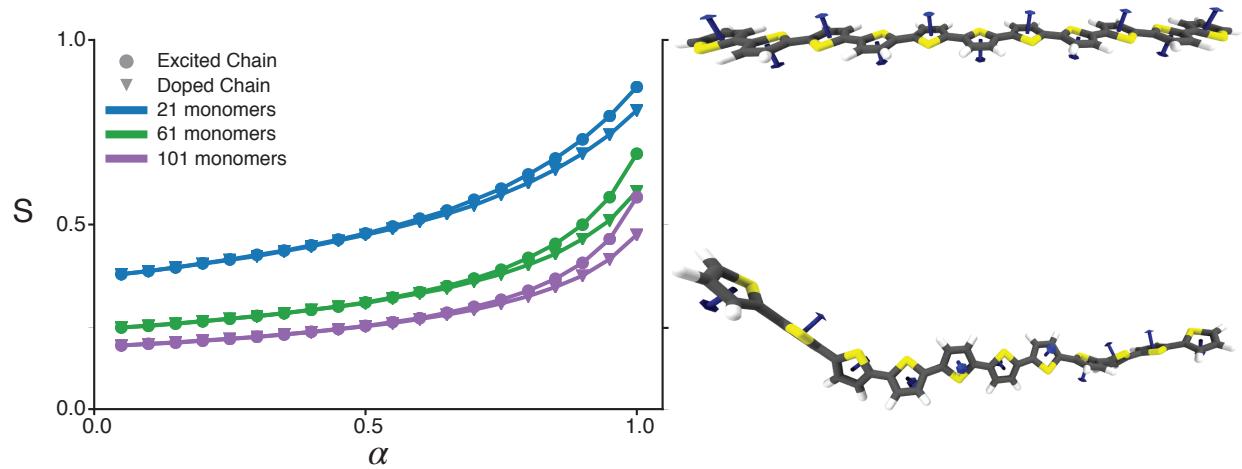


Figure 2.5: Left) Chain planarity (S) as a function of doping and excitation (α). When $S = 0$ all thiophene rings have equal probability of facing any direction, whereas when $S = 1$ the chain is completely planar. Right) Examples of $S = 1$ and $S \sim 0.2$

polarons and their interactions to determine the proper ordering/grouping of doped or excited torsion angles along the chain for non-integer values of α . We note that ordering does not impact the calculation of S due to the use of the globally defined director. Furthermore, the conjugation length is also dependent on the torsion angle at which conjugation is substantially disrupted (i.e. when the energy barrier to carrier transport is well above thermal fluctuations). Previously, Bredas et al. suggested that torsional configurations which deviate more than 30-40° from planar disrupt electronic properties in aromatic conjugated polymers such as PT and PPy.[9] Regardless of the ability to determine the conjugation length, the order parameter S provides evidence that carrier mobility increases with increasing doping or excitation due to torsional rearrangements.

Material Design Strategies

Our results offer a microscopic explanation for the increase of electronic conductivity due to sequential doping, which preferentially dopes amorphous domains in conjugated polymer materials.[16, 44] Compared to other techniques sequential doping improves conductivity, and this has been attributed to an increase in the conjugation length of amorphous chains.[16] We find that planarity—a measure of conjugation length—increases with doping because of electronic structure and torsional rearrangements. In sum, amorphous chain planarization leads to an increase in carrier mobility and ultimately an improvement of the material’s electronic conductivity.

Another method intended to improve electronic conductivity recommends an ultraviolet (UV) treatment to order conjugated polymers in solution before film synthesis.[13] Organic field-effect transistors made with P3HT films that were pretreated with UV irradiation (~ 5 mins) exhibited higher carrier mobility compared to those not pretreated. The improvement in mobility was attributed to “increased molecular order,” and it was postulated that intrachain planarization induced by excitation caused more interchain $\pi - \pi$ stacking interactions eventually leading to aggregates in solution. These aggregates persisted in the resulting films,[13] and presumably more uninterrupted conjugation pathways were present. Although unknowns persist about $\pi - \pi$ stacking and polymer-solvent interactions, it is encouraging that device level results agree with the fundamental premise that excitation causes chains to become more planar and that this knowledge can be leveraged to improve materials performance.

Finally we comment on side chain engineering as a design strategy. Many aromatic conjugated polymers are decorated with side chains, for example P3HT has a PT backbone with a hexyl side chain. Son et al. synthesized P3HT and PT random copolymers to investigate how the ratio impacted carrier mobility. It was found that introducing more PT reduced crystallinity, increased out-of-plane $\pi - \pi$ stacking, and improved mobility.[75] For our torsion potential model we assume that chains are able reach a thermodynamically favorable conformation, however in certain circumstances bulky side chains may limit backbone torsional rearrangement upon doping or excitation. Thus, lowering side chain density along the polymer backbone may provide a useful strategy to increase the likelihood that a doped or excited backbone torsion angle assumes a planar configuration. A potential exception to this analysis would include bulky side chains that promote planarity in ground-state chains.[66]

2.4 Conclusions

The structural properties of amorphous conjugated polymers change as a function of doping and excitation. Initially, aromatic chains undergo a localized electronic structure rearrangement where the bonding pattern is transformed from aromatic to quinoidal. Consequently, the bridge double bond character present in the quinoidal structure drives torsional rearrangement. This description is supported by the reduction in bridge bond lengths as well as the preference for planar configurations in the associated doped and excited-state torsion potentials. To connect electronic structure changes with doped and excited polymer structure we developed a torsion potential model. Our model reproduced experimental persistence lengths for ground-state polythiophene, and the experimental trends in persistence length for doped and excited chains. Chain planarity, which is an important structural property for carrier mobility, monotonically increases with the level of doping or excitation. Notably, our results demonstrated that planar polythiophene conformations can be highly non-linear due to cis torsion configurations. We find that the fraction of cis torsion angles largely dictates the persistence length and end-to-end distance of both doped and excited chains. Excited chains contain a larger fraction of cis torsion angles as compared to doped chains

which explains how the trends in persistence length diverge, whereas the trends in planarity are similar. Furthermore, amorphous chain planarization induced by doping and excitation corresponds to enhanced conjugation and ultimately an increase in carrier mobility and electronic conductivity. While more research is needed to adequately characterize doped and excited amorphous chains, the structural insights reported here can be used to interpret characterization data and to advance design strategies aimed at tuning electronic properties in conjugated polymers.

2.5 Methods

Torsion Potential Model

The overall torsion potential model methodology has been described by others,[88, 18] but due to our alterations and inclusion of doping and excitation a description is included. A schematic of model is displayed in Fig. 2.1. To start, torsion potentials ($V(\phi)$) for the ground, doped, and excited states were calculated using quantum chemistry. Torsion potentials were fitted using the Ryckaert-Bellemans function (eq. 2.1). Details of the fitting procedure and data can be found in the supporting information (SI Section ??). Each torsion potential was used to generate a room temperature (300 K) Boltzmann probability distribution (eq. 2.2) for the full range of torsion angles (-180° to 180° with a mesh of 0.1 degrees). The Boltzmann probabilities ($p(\phi)$) were then summed to give cumulative probabilities. Cumulative probabilities (ranging from 0-1) provide a unique torsion angle (ϕ) mapping that enabled torsion angles to be selected by generating random numbers between 0 and 1. As a result, chain conformations were defined by generating a set of random numbers that correspond to a set of torsion angles. Doping and excitations were introduced by randomly placing doped or excited torsion angles along the ground-state chain. Doped or excited torsion angles were drawn from their respective cumulative probabilities using random numbers similar to the ground state procedure. The variable α , which represents the level of doping or excitation, is obtained as the fraction of doped or excited torsion angles. Unless otherwise noted all ensembles at different values of α were sampled with 50,000 conformations.

$$V(\phi) = \sum_{n=0}^5 c_n \cos^n(\phi) \quad (2.1)$$

$$p(\phi) = \frac{e^{-V(\phi)/k_B T}}{\sum_{\phi} e^{-V(\phi)/k_B T}} \quad (2.2)$$

The adopted torsion potential model assumes that nearest neighbor torsion angles are independent, and that the torsion potential alone governs single chain conformations. Self

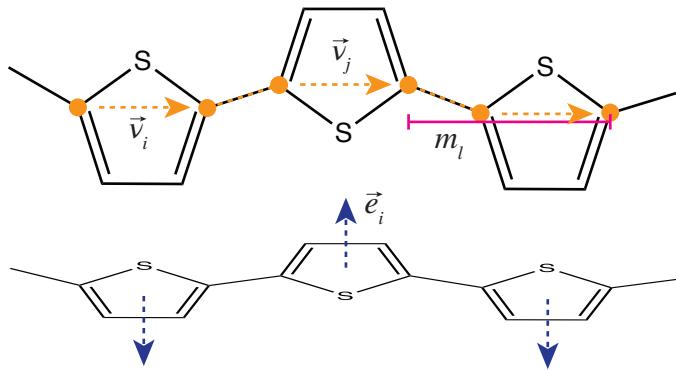


Figure 2.6: Top) Backbone vectors (\vec{v}) and average monomer length (m_l) for PT. Bottom) Thiophene ring normal vector (\vec{e})

avoidance was not explicitly enforced in our model. We assumed all ground-state chains to be in equilibrium and doped and excited chains in steady-state, signifying that a chain can reach a thermodynamically favorable conformation (i.e. no kinetic limitations). Because we were primarily concerned with equilibrium or steady-state structural properties, we did not consider the torsional dynamics associated with doping or excitation. Doped and excited steady-states require that the number of doped or excited torsion angles remain constant. The steady-state approximation is motivated by recent findings that torsional relaxation upon excitation occurs very rapidly, whereas the torsional relaxation of the reverse process occurs slowly.[11, 84] Further explanation of the model and its implementation (i.e. the code used) are available in SI Section ??.

Chain Properties

To characterize polymer chain length, we used the persistence length and the root-mean-square end-to-end vector $\sqrt{\langle R^2 \rangle}$ or simply end-to-end distance. In the torsion potential model end-to-end distance was determined by the scalar displacement from the first carbon atom in the chain to the last carbon atom in the chain. Persistence length (l_p) was calculated using the tangent-tangent correlation function (eq. 2.3), a relationship that can be derived from the worm-like chain (WLC) model, where \vec{v}_i represents the backbone vector i and its correlation with \vec{v}_j the backbone vector j. Angle brackets $\langle \rangle$ represent ensemble averages. The contour length (L) of a chain was defined as length of a trans chain (all trans torsion angles, shown in Fig. 2.4B), and is approximately the number of monomers (N) times the average monomer length (m_l), $L \approx m_l N$. Backbone vectors, normal vectors, and average monomer length specific to PT are shown in Fig. 2.6.

$$\left\langle \vec{\nu}_i \cdot \vec{\nu}_j \right\rangle = \exp \left(-\frac{L}{\chi l_p} \right) \quad (2.3)$$

The scaling factor χ in eq. 2.3 is equal to 1 for a 3-dimensional (3D) WLC and is equal to 2 for a 2-dimensional (2D) WLC.^[5] By comparing the $\sqrt{\langle R^2 \rangle}$ for the 3D-WLC, the 2D-WLC, and the torsion potential model (Fig. ??, ??, ??) we find that for the torsion potential model χ lies between 1 and 2 in all cases. As a result, χ was fit for all α values and the fit χ values were used to determine the persistence length. More details on χ and persistence length calculations are provided in Section ?? of the SI.

Planarity was also considered in the description and analyses of chain structure. For our purposes, planarity is defined by the orientational order parameter S (eq. 2.4),^[2] which is used to quantify molecular orientation in liquid crystals. The variable θ represents the angle between a thiophene ring's unit normal vector (\hat{e}) (Fig. 2.6) and the director. The director for a chain is a unit vector that represents the most common direction of (\hat{e}), something akin to the average direction of the rings along the chain. See SI Section ?? for details on how S and the director were computed using the orientational order tensor (Q).

$$S = \frac{1}{2} \left\langle 3 \cos^2 \theta - 1 \right\rangle \quad (2.4)$$

Quantum Chemistry Calculations

Quantum chemistry calculations were used to generate dimer torsion potentials and other structural information. All calculations were performed using QChem software.^[71] Unless otherwise noted, calculations were done in vacuum and the level of theory utilized was the hybrid functional ω B97M-V with basis sets def2-QZVPPD and def2-TZVPPD for ground state and doped/excited states respectively.^[56, 79] Hybrid DFT functionals were chosen over MP2 methods because of spin contamination issues^[69], and basis set sensitivity. Additionally, excited state (T1) calculations were carried out using unrestricted open shell DFT (UO), as both UO and restricted open shell (RO) DFT reproduce experimental results better than TDDFT for conjugated molecules.^[38] Further discussion and comparison of T1 RO-DFT, UO-DFT, and TDDFT calculations can be found in Table ???. The general procedure for all torsion potentials was to do an initial geometry optimization of the dimer, then rotate the central or bridge torsion angle between rings to the angle of interest, and finally run a constrained optimization with the C-C-C-C torsion angle of interest fixed. The last two steps were preformed over the range of unique torsion angles.

All doped and excited state calculations were carried out using unrestricted open shell (UO) DFT. Both UO and restricted open shell (RO) DFT reproduce experimental results better than TDDFT for excited conjugated molecules.^[38] A comparison of T1 RO-DFT, UO-DFT, and TDDFT calculations can be found in Table ???. It is important to note that RO-DFT or UO-DFT calculations are only reliable for clearly defined HOMO to LUMO

CHAPTER 2. STRUCTURAL CHANGES IN DOPED AND EXCITED CONJUGATED POLYMERS 14

transitions, which encompassed all of our T1 torsional configurations with energies relevant for room temperature sampling. However in PT, the nature of the transition at torsion angles around -90° and 90° is affected by other energy levels. As a result, torsion angles around -90° and 90° may benefit from refinement with a higher level of theory.

Chapter 3

Aromaticity as a Guide to Planarity in Conjugated Molecules and Polymers

3.1 Introduction

Organic semiconductors offer unique blends of physical and electronic properties along with the processability and fabrication potential of polymers and small molecules.[52, 76] This combination opens up countless opportunities for new functional materials that can be tailored for specific applications.[58, 60, 74, 78] One successful strategy for tuning molecular properties is adding pendent groups to the conjugated backbone; these “noncovalent locks” control molecular structure by inducing nonbonded interactions.[43, 15, 20, 41] The goal is to create structures that prefer coplanar torsional configurations that maximize electron delocalization across the molecule or polymer (i.e. conjugation), and as a result improve electronic properties such as carrier mobility.

While noncovalent locks have proven to be effective at creating planar structures, the exact nature of the interactions leading to planarity remain difficult to disentangle. A few reports have attempted to isolate and identify the fundamental interactions behind noncovalent locking systems. For instance, Jackson et al. demonstrated that nontraditional hydrogen bonding (i.e. hydrogen bonding that involves less electronegative atoms such as C, S, and Cl) can play a predominant role in stabilizing planar configurations.[43] Nevertheless, many locking molecules such as 3,4-ethylenedioxythiophene (EDOT) and fluorinated thiophenes—which are utilized in state-of-the-art conjugated molecules and polymers[86, 37, 82, 32, 33, 45, 53]—do not involve nontraditional hydrogen bonding. Conboy et al. confirmed the importance of heteroatom interactions in poly-EDOT (PEDOT) and similar molecules, but stated that a precise description of torsional energetics was unclear and speculated that electrostatics were responsible for the observed planarity.[20]

Aromaticity is a common chemical descriptor that can be used to simplify some of the underlying physics and provide novel insights into torsional energetics. A key objective of this communication is to highlight how the competition between aromaticity and conjugation[40,

[48, 41] influences planarity in organic electronic materials. We show that the introduction of popular noncovalent locks modifies aromaticity and drives structures towards planarity. Finally, we identify the specific hyperconjugation interaction that alters aromaticity and determines planarity.

3.2 Results and Discussion

An illustrative example of the balance between ring aromaticity and conjugation is the torsion potential of bithiophene (BT) (Fig. 3.1). Dimers provide a computationally efficient and accurate representation of the torsion potential and trends in aromaticity observed in larger conjugated polymers (See SI)[25] and hence are used throughout this work. The aromaticity of individual rings is quantified using the multicenter bonding index (MCI),[35, 34] and the nucleus-independent chemical shift (NICS)[26, 14] (see SI). We represent conjugation semi-quantitatively as the normalized relative bond length of the bridge C-C bond between rings; the rational being configurations with shorter bridge bonds are more conjugated.[24, 27] Figure 1 (left side) clearly shows that the stabilizing effects of aromaticity and conjugation are in direct competition with one another. This agrees with a simple description based on atomic orbitals, where planar structures (0° cis and 180° trans) exhibit the most p_z -orbital overlap (π -bonding) and afford the most electron delocalization across the molecule. Whereas the torsioned structure at 90° will exhibit the least electron sharing between rings, and it possesses the highest ring aromaticity or electron delocalization within a ring. The non-planar global minimum (150°) in the torsion potential appears to be the balance between these two driving forces.

To test this hypothesis we removed aromaticity by hydrogenating the terminal C=C double bonds, leaving intact the conjugation across the rings (right side of Fig. 3.1). Once aromaticity was removed the torsional energetics essentially mirrored conjugation, and most importantly the global minimum in the torsion potential shifted to the planar 180° configuration. It is noteworthy that the inter-ring H \cdots S distance is reduced in hydrogenated bithiophene (hBT) (2.78\AA in the 180° configuration) compared to BT (2.93\AA in the 180° configuration), which reduces concern that the 150° torsional minimum in BT is due to steric repulsion between H \cdots S. This conclusion is supported with through-space calculations and noncovalent interaction (NCI) analysis[46, 21] in the SI. Establishing aromaticity as a driving force in torsional energetics is fundamental for understanding structure; additionally, if aromaticity can be modified or controlled it may represent a design opportunity.

Having demonstrated the important role of aromaticity in directing torsion angles, we were motivated to explore the role of aromaticity in known planar systems with noncovalent locks. We discovered a number of reported noncovalent locks modify aromaticity. As observed in the top of Fig. 3.2 both 3,3'-difluorobithiophene (F2-BT) and bis-EDOT (BEDOT) exhibit a coplanar torsional minimum at 180° accompanied by an increase in aromaticity near 180° . As expected, conjugation is minimized at 90° and a maximized at 180° , it has been left out of Fig. 3.2 for clarity. For torsional energetics the magnitude of aromaticity is less important

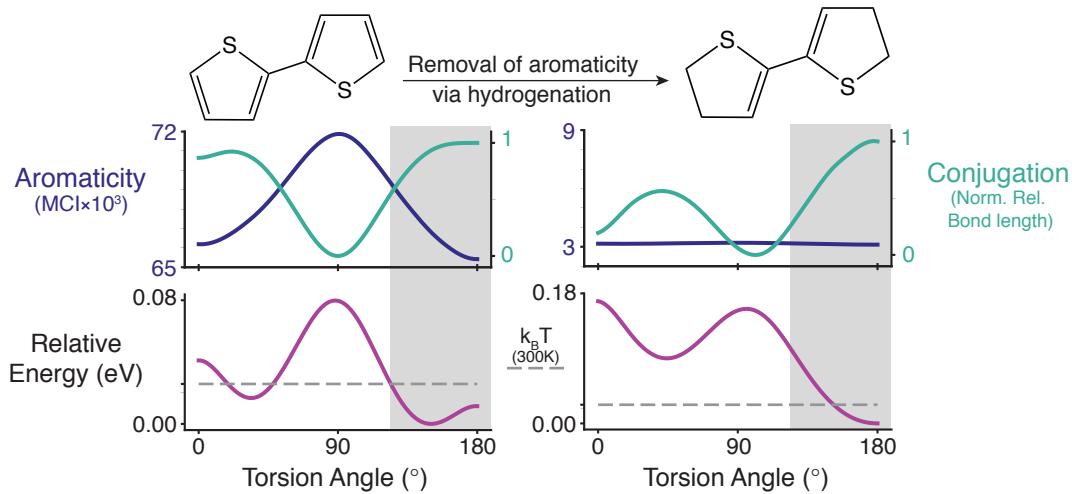


Figure 3.1: Ring aromaticity, molecular conjugation, and relative energies are plotted as a function of torsion angle for bithiophene (BT) and hydrogenated bithiophene (hBT). Both BT and hBT structures are represented in the 180° (trans) configuration. Aromaticity and conjugation are directly opposed in BT and the balance between the two driving forces results in a non-planar torsional minimum around 150° . Hydrogenation of the terminal C-C double bonds essentially reduces aromaticity to zero, while preserving conjugation across the two rings. With aromaticity removed in hBT, torsional energetics mirror conjugation and there is a planar minimum at 180° . Aromaticity is defined as the multicenter bonding index ($MCI \times 10^3$) for one C-C-S-C-C thiophene ring. Only one ring is displayed because both BT and hBT are symmetric molecules. Conjugation is quantified as the normalized relative bridge C-C bond length. A value of 1 represents the shortest bond length and the highest conjugation, whereas 0 represents the longest bond and lowest amount of conjugation.

than the change in aromaticity. For example, if aromaticity is constant across all torsion angles there is no torsional driving force. As a result, we are interested in the change in aromaticity between $90\text{-}180^{\circ}$.

To further investigate the modification of aromaticity we systematically added fluorine at different ring positions (bottom of Fig. 3.2). Notably, aromaticity increases near 180° in ring 2 (the ring without F added) of 3F-BT similarly to that of BEDOT and F2-BT in the top of Fig. 3.2. With only one added fluorine the aromaticity of both ring 1 and ring 2 need to be characterized because the molecule is no longer symmetric. When fluorine is added to ring 1—regardless of the position—it reduces the magnitude of aromaticity but preserves the shape of the curve (bottom left of Fig. 3.2), essentially reducing the underlying function by a constant. This is consistent with earlier reports that adding electron withdrawing substituents to an aromatic ring reduces the overall aromaticity.^[51] Naively, one might expect all thiophene rings without F added to be similar, and this is largely true for ring 2 of BT and

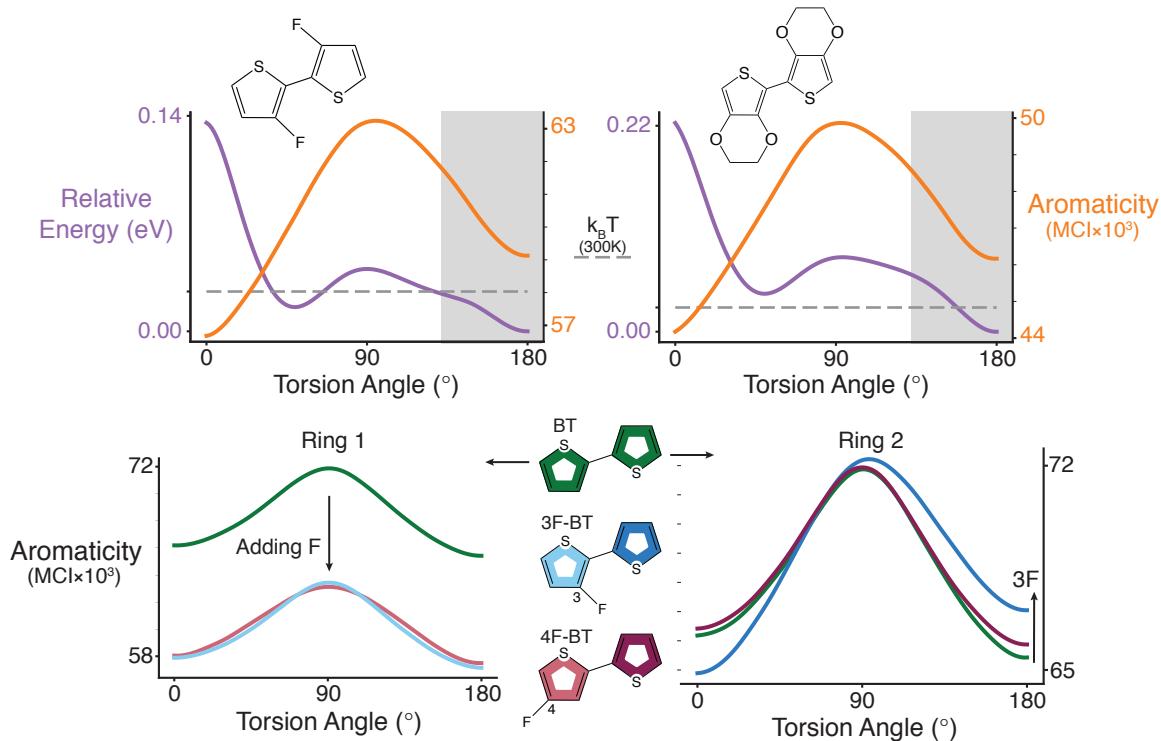


Figure 3.2: (Top) Torsional relative energies and aromaticity are plotted for F2-BT and BEDOT. In both systems aromaticity is increased near 180° and this corresponds to an energetic minimum. (Bottom) Ring 1 and ring 2 aromaticities are plotted against torsion angles for BT, 3F-BT, and 4F-BT. Both rings are plotted because 3F-BT and 4F-BT molecules are no longer symmetric as is BT. For ring 1 the addition of F—regardless of the position—reduces the magnitude of aromaticity by a constant, but preserves the shape of the BT curve. The ring 2 curves are similar for 4F-BT and BT, however, ring 2 of 3F-BT deviates in shape and aromaticity is increased near 180° similar to the plots in the top of figure.

4F-BT but as mentioned ring 2 aromaticity is modified in 3F-BT. This result indicates that there is a noncovalent inter-ring interaction between $F \cdots S$ causing the change in aromaticity.

Using Natural Bonding Orbital (NBO) analysis we identify the key interaction responsible for the modification of aromaticity and for stabilizing the planar 180° configuration (Fig. 3.3). Our through-space calculations for $F \cdots S$ and $O \cdots S$ indicate that both would be repulsive at the respective relaxed separation distance present in the 180° configuration of F2-BT and BEDOT (see SI). Thus, it is clear that some other interaction involving $X \cdots S$ is stabilizing the steric effects in order for the 180° configuration to be energetically favorable. NBO perturbation analyses revealed a 3-center-2-electron interaction between a heteroatom lone pair and a C-S antibonding orbital (σ_{C-S}^*) pictured in the top of Fig. 3.3. Details on specific

energies are provided in the SI. Similar interactions have been reported for the association of supramolecules.[22] Conboy et al. mentioned this type of interaction as a possible source of attraction in BEDOT-like molecules, but dismissed it due to a lack of bond length correlations across a series of related molecules.[20]

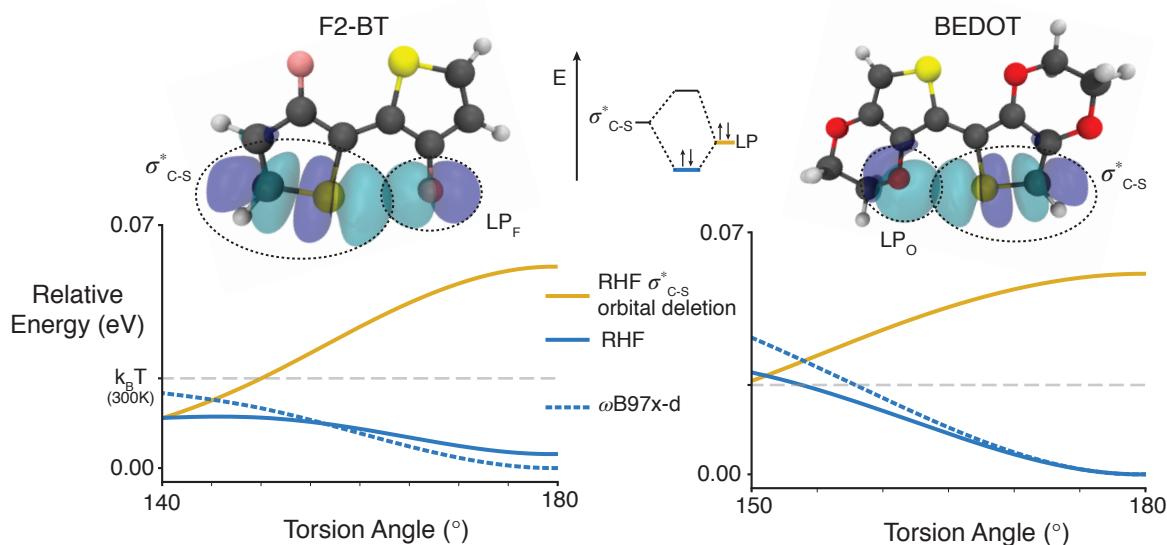


Figure 3.3: (Top) Isosurface plots of the overlap between C-S antibonding (σ^*_{C-S}) and F or O lone pair (LP) natural bonding orbitals in F2-BT and EDOT (isovalue ≈ 0.03). The orbital overlap leads to a stabilizing hyperconjugation interaction depicted in between the isosurface plots. (Bottom) The torsion potentials of F2-BT and BEDOT are displayed for ω B97x-D, RHF, and RHF with the σ^*_{C-S} orbital removed. RHF and ω B97x-D are qualitatively similar, both having a minimum at 180°. When the σ^*_{C-S} orbital is deleted from the Fock matrix (using NBO6) the hyperconjugative stabilization is no longer present and without that interaction the molecules are no longer planar.

In order to confirm the importance of the 3-center-2-electron interaction we utilized the NBO deletion method[36], which has been used previously to deconvolute torsional energetics.[64] Because the NBO deletion method necessitates the use of restricted Hartree-Fock (RHF) we recalculated the torsion potentials with RHF to ensure qualitatively similar behavior to the higher level of theory (ω B97x-D). Then using the RHF deletion method, we removed the C-S antibonding orbitals (σ^*_{C-S}) on both rings, which eliminates hyperconjugation. Remarkably, removing hyperconjugation altered the torsional energetics in both BEDOT and F2-BT such that the planar 180° configurations are no longer favorable (as shown in Figure 3), most likely due to the steric repulsion that exists. We characterize these as hyperconjugation interactions because they result in electron delocalization across the molecule and there is a history of hyperconjugation impacting torsional energetics.[64, 65] This result provides strong

evidence that hyperconjugation is the critical interaction responsible for the locking behavior in these molecules and polymers.

3.3 Conclusion

Using a variety of computational techniques we have demonstrated that aromaticity is a useful descriptor to help understand the complex interactions which lead to the structure of conjugated molecules and polymers. In general, aromaticity is stabilizing and energetically favorable, and in extended conjugated molecules and polymers ring aromaticity prefers torsioned or non-planar configurations because it confines delocalized electrons within a ring instead of delocalizing them across the entire molecule or polymer. As such, aromaticity directly competes with conjugation, also known to be stabilizing and energetically favorable. BT is an ideal system to exemplify this competition, and ultimately we identify a balance between the two factors that results in a non-planar minimum energy configuration. Planarity and conjugation are vital for the electronic properties of conjugated materials so minimizing the driving force from aromaticity is industrially relevant. We find that aromaticity can indeed be beneficially modified through pendent group additions or noncovalent locks such as F2-BT and BEDOT. In both examples, a heteroatom interacts with an adjacent ring and increases its aromaticity at torsional angles near 180° where the atoms are the closest together. To probe the exact nature of this interaction we identified and removed hyperconjugation between a heteroatom (i.e. F and O) lone pair and the C-S antibonding orbital on the adjacent ring, concluding that hyperconjugation is responsible for the changes in aromaticity and for the resulting planarity or locking behavior. We anticipate that the structural insights and methods presented here are applicable to a wide range of conjugated molecules and polymers, and will open the door to new and unforeseen advances in our ability to design functional organic electronic materials.

3.4 Computational Methods

All quantum chemistry calculations were performed with Gaussian 16 unless otherwise noted.^[31] The default level of theory was ω B97x-D with the def2-TZVPP basis set.^[12, 79] The general procedure for calculating torsion potentials started with an unconstrained geometry relaxation followed by a frequency calculation to ensure no substantial imaginary frequencies existed. Then the relaxed geometry was rotated around the central C-C bond, fixing the C-C-C-C torsion every 10° for a constrained geometry optimization. An additional torsional constraint was used for hydrogenated calculations (See SI). MCI aromaticities were computed with the natural atomic orbital basis from NBO6 for all 5 member (C-C-S-C-C) rings at each torsional geometry using Multiwfn.^[54] NBO analysis was performed using NBO6.^[36] All RHF and RHF NBO orbital deletions were done with Gaussian 09^[30] and NBO6 again using the def2-TZVPP basis set. RHF NBO orbital deletions were single point

calculations utilizing relaxed RHF geometries. Isosurface images were made with VMD,[42] and all plotting utilized Matplotlib and cubic spline interpolation via SciPy.[47]

Chapter 4

Conclusion

Conclude here

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Appendix A

Appendix for Structural Changes in Doped and Excited Conjugated Polymers

A.1 Polythiophene Torsion Potentials

Torsion Potential Data and Initial Structures

Table A.1: Ground-state Thiophene Dimer Initial Structure

	Atom	X (Å)	Y (Å)	Z (Å)
1	S	-0.0023723	-0.0560977	-0.0300969
2	C	1.7070035	-0.0292241	-0.0145267
3	H	2.2421009	-0.0503556	0.9188681
4	C	2.2188238	0.0166957	-1.2731976
5	H	3.2760435	0.0396095	-1.4857363
6	C	1.2080458	0.0437755	-2.2700460
7	H	1.4022626	0.1035054	-3.3303301
8	C	-0.0534481	0.0159971	-1.7485209
9	C	-1.3283732	0.0357503	-2.4552048
10	C	-2.5140867	0.5793303	-2.0518483
11	H	-2.6304470	1.0993723	-1.1131149
12	C	-3.5508397	0.4152358	-3.0079307
13	H	-4.5565336	0.7819288	-2.8760054
14	C	-3.1332923	-0.2472315	-4.1192789
15	H	-3.7048930	-0.4997928	-4.9952883
16	S	-1.4859744	-0.6908589	-4.0068121

Table A.2: Ground-state Thiophene Dimer Torsion Data

	Torsion Angle	Rel. Energy (eV)	Abs. Energy (Hartree)
1	0.0	0.04598	-1104.84987203842
2	10.0	0.03979	-1104.85009939477
3	20.0	0.02779	-1104.85054035879
4	30.0	0.01928	-1104.85085335093
5	40.0	0.01868	-1104.85087543253
6	50.0	0.02689	-1104.85057349252
7	60.0	0.04200	-1104.85001836446
8	70.0	0.05898	-1104.84939439490
9	80.0	0.07241	-1104.84890093182
10	90.0	0.07646	-1104.84875201328
11	100.0	0.06924	-1104.84901713984
12	110.0	0.05278	-1104.84962222807
13	120.0	0.03288	-1104.85035334414
14	130.0	0.01530	-1104.85099955470
15	140.0	0.00358	-1104.85143006908
16	150.0	0.00000	-1104.85156180070
17	160.0	0.00326	-1104.85144196165
18	170.0	0.00927	-1104.85122115615
19	180.0	0.01234	-1104.85110839823

Table A.3: Doped-state Thiophene Dimer Initial Structure

	Atom	X (Å)	Y (Å)	Z (Å)
1	S	0.0003979	0.4373270	-0.0633642
2	C	1.6743230	0.2163099	-0.0571461
3	H	2.2287328	0.3339913	0.8611866
4	C	2.1929799	-0.1115590	-1.3041171
5	H	3.2426659	-0.2866798	-1.4795321
6	C	1.2098407	-0.1839581	-2.2716885
7	H	1.3925319	-0.4251174	-3.3088107
8	C	-0.0772964	0.0912069	-1.7653271
9	C	-1.2859459	0.1035335	-2.4670641
10	C	-2.5730754	0.3787571	-1.9607149
11	H	-2.7557610	0.6199609	-0.9236020
12	C	-3.5562300	0.3062435	-2.9282622
13	H	-4.6059215	0.4813222	-2.7528378
14	C	-3.0375815	-0.0216838	-4.1752213
15	H	-3.5920046	-0.1394621	-5.0935336
16	S	-1.3636358	-0.2425520	-4.1690348

Table A.4: Doped-state Thiophene Dimer Torsion Data

	Torsion Angle	Rel. Energy (eV)	Abs. Energy (Hartree)
1	0.0	0.02079	-1104.50938633204
2	10.0	0.02825	-1104.50911231215
3	20.0	0.05223	-1104.50823104848
4	30.0	0.09371	-1104.50670665615
5	40.0	0.15812	-1104.50433961960
6	50.0	0.24644	-1104.50109374877
7	60.0	0.35673	-1104.49704060708
8	70.0	0.48820	-1104.49220922909
9	80.0	0.63920	-1104.48666033352
10	90.0	0.78498	-1104.48130300611
11	100.0	0.62139	-1104.48731456600
12	110.0	0.47554	-1104.49267465589
13	120.0	0.34797	-1104.49736261553
14	130.0	0.24010	-1104.50132673110
15	140.0	0.15423	-1104.50448240244
16	150.0	0.08729	-1104.50694235511
17	160.0	0.03966	-1104.50869281167
18	170.0	0.01087	-1104.50975071487
19	180.0	0.00000	-1104.51015031856

Table A.5: Excited-state Thiophene Dimer Initial Structure

	Atom	X (Å)	Y (Å)	Z (Å)
1	S	-0.0180675	0.4466192	-0.0408593
2	C	1.6926804	0.2166109	-0.0439241
3	H	2.2550459	0.3305548	0.8671136
4	C	2.1935848	-0.1115653	-1.3030670
5	H	3.2449313	-0.2870510	-1.4774923
6	C	1.2341910	-0.1883271	-2.2796908
7	H	1.4178092	-0.4288461	-3.3154027
8	C	-0.1008011	0.0925904	-1.7763147
9	C	-1.2624454	0.1021336	-2.4560715
10	C	-2.5974302	0.3830769	-1.9527024
11	H	-2.7810468	0.6236319	-0.9169985
12	C	-3.5568312	0.3062823	-2.9293227
13	H	-4.6081778	0.4817637	-2.7548939
14	C	-3.0559380	-0.0219757	-4.1884438
15	H	-3.6183064	-0.1359654	-5.0994740
16	S	-1.3451782	-0.2518931	-4.1915259

Table A.6: Excited-state Thiophene Dimer Torsion Data

	Torsion Angle	Rel. Energy (eV)	Abs. Energy (Hartree)
1	0.0	0.01269	-1104.69509558720
2	10.0	0.02498	-1104.69464387418
3	20.0	0.06486	-1104.69317837941
4	30.0	0.13225	-1104.69070196155
5	40.0	0.22992	-1104.68711247641
6	50.0	0.36069	-1104.68230686926
7	60.0	0.50986	-1104.67682512101
8	70.0	0.64448	-1104.67187782963
9	80.0	0.75853	-1104.66768637840
10	90.0	0.84183	-1104.66462531896
11	100.0	0.76183	-1104.66756522231
12	110.0	0.65961	-1104.67132193500
13	120.0	0.53077	-1104.67605665532
14	130.0	0.38036	-1104.68158410041
15	140.0	0.24551	-1104.68653968278
16	150.0	0.13895	-1104.69045559904
17	160.0	0.06376	-1104.69321900264
18	170.0	0.01692	-1104.69494025977
19	180.0	0.00000	-1104.69556201328

Ground-state Torsion Potentials at Different Levels of Theory

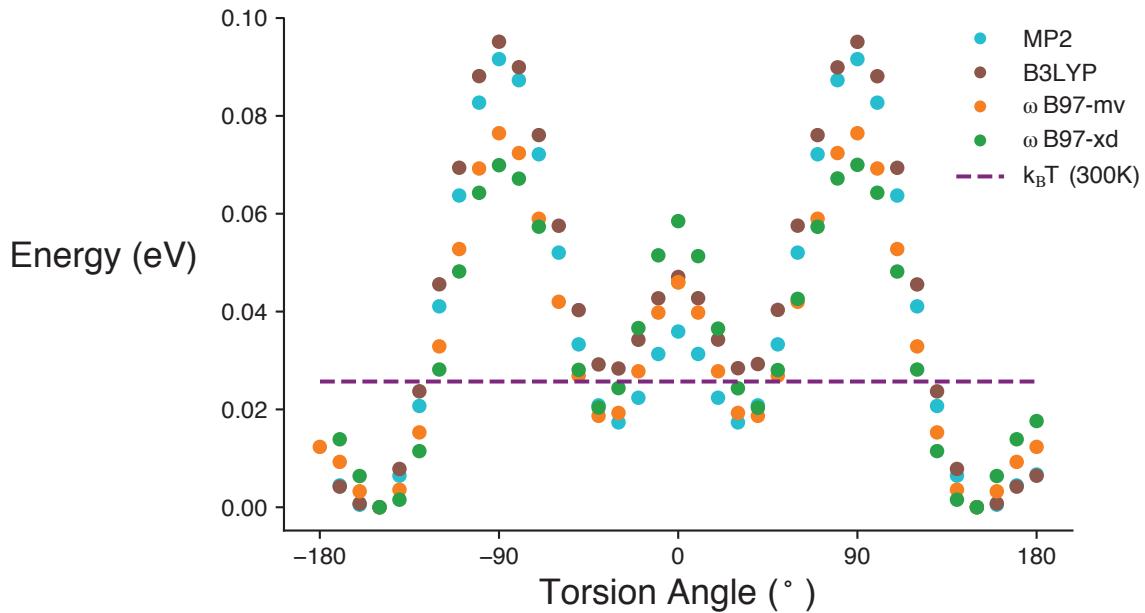


Figure A.1: Ground-state torsion potential at different levels of theory. MP2 basis set: cc-pVTZ, B3LYP and ω B97-xd basis set: 6-31++G**, ω B97-mv basis set: def2-QZVPPD

The Effect of Chain Length on Ground-state Torsion Angles

Different polythiophene (PT) chain lengths were optimized at the RI-MP2 level (Figure A.7). In all instances the optimized structures had non-planar central torsion angles corresponding to minima observed in Figure A.1. Additionally, the energy of optimized planar (trans) configurations were higher than that of optimized non-planar configurations. This evidence supports DuBay et al. in their claim that the torsion potential of conjugated polymers such as PT can be approximated by the dimer torsion potential if an appropriate level of theory, basis set, and optimization procedure are used.[25]

Table A.7: Ground-state Optimized Geometries

Number of Monomers	Trans Geometry Abs. Energy (Hartree)	Optimized Geometry Abs. Energy (Hartree)	Optimized Central Torsion Angle (°)
2	-1103.35246329362 ^a	-1103.35284395916 ^a	22
4	-2205.26456300358 ^b	-2205.26519616574 ^b	161
8	—	-4409.36496730408 ^b	159

^a Theory: RI-MP2 basis set: cc-pVQZ^b Theroy: RI-MP2 basis set: cc-pVTZ

Appendix B

Appendix for Aromaticity as a Guide to Planarity in Conjugated Molecules and Polymers

B.1 Different Length Polymer Chains

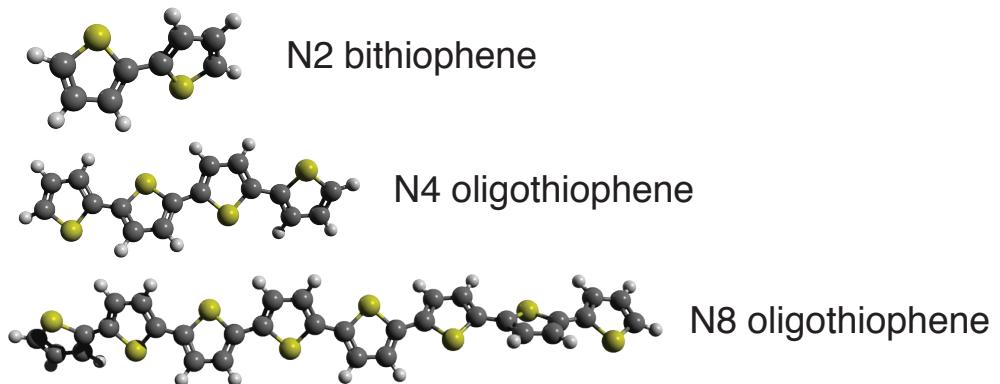


Figure B.1: Different length oligomers of thiophene.

Comparison of Torsion Potentials

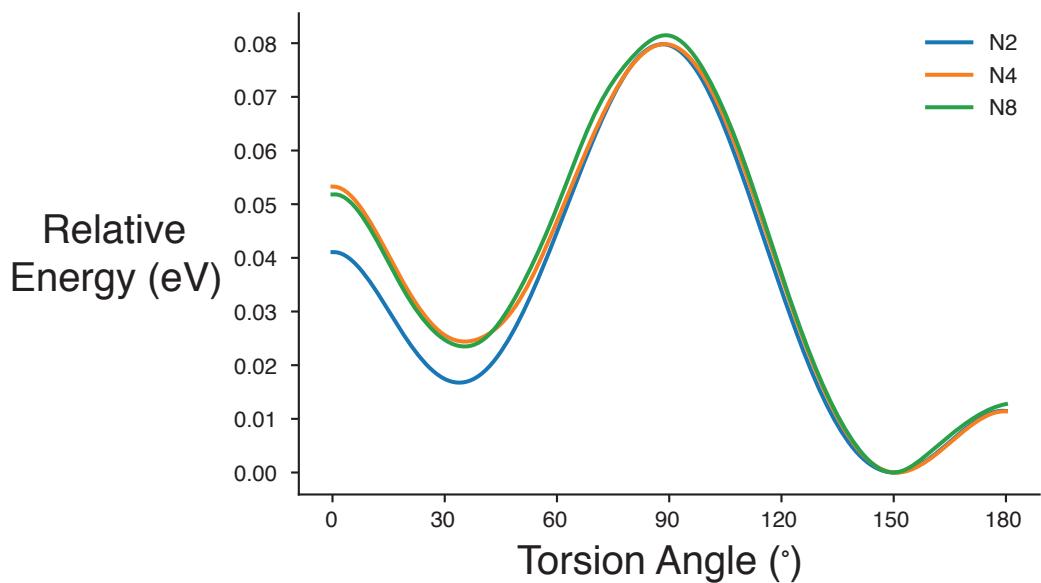


Figure B.2: The torsion potential of N2, N4, and N8 thiophene oligomers. All calculations were performed using the ω B97x-D functional. The N2 torsion potential was calculated with the def2-TZVPP basis set, while N4 and N8 utilized the 6-31++G**[39] basis set to reduce to the computational cost. The deviation of N2 from both N4 and N8 between 0 and 50° is likely due to the different basis sets employed.

Comparison of NICS Aromaticity

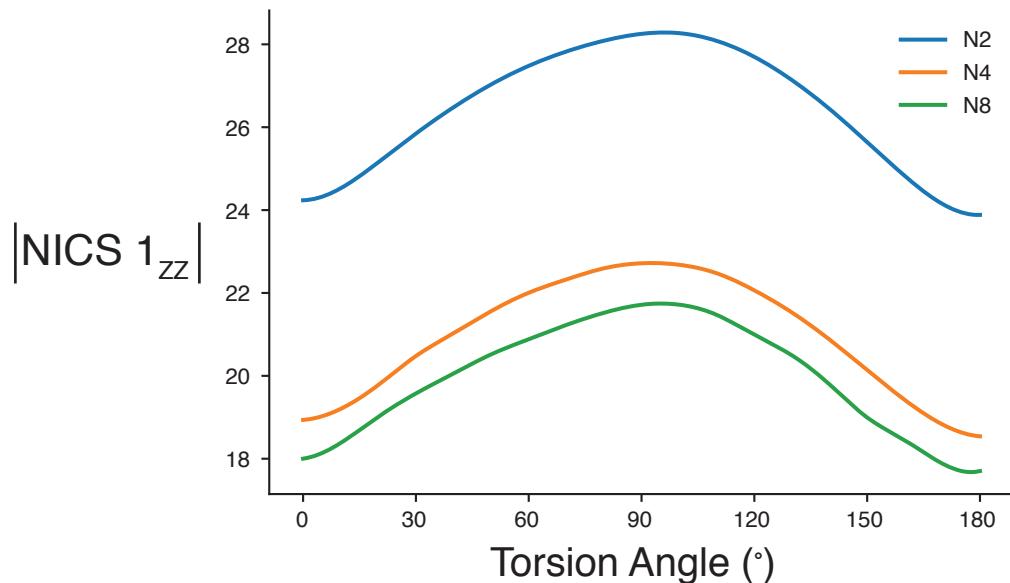


Figure B.3: N2, N4, and N8 absolute NICS 1_{zz} values as a function of torsion angle. The magnitude of NICS values decrease with chain length, and we expect that the values will converge once a certain chain length is reached. While the magnitude decreases the overall trend as a function of torsion angle is consistent, which allows N2 to represent larger chains.

B.2 Comparision of MCI and NICS Aromaticity Values

BT

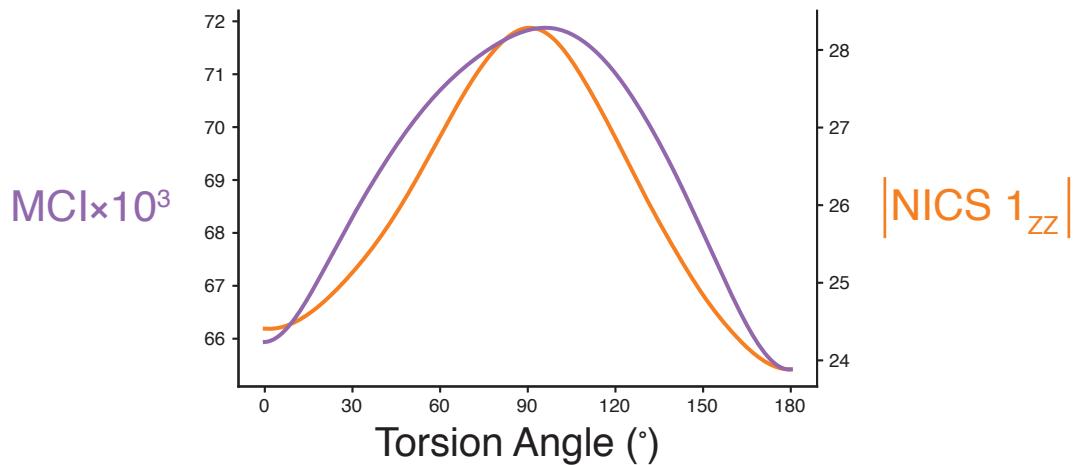


Figure B.4: Comparison of the aromaticity indexes MCI and NICS for BT.

hBT

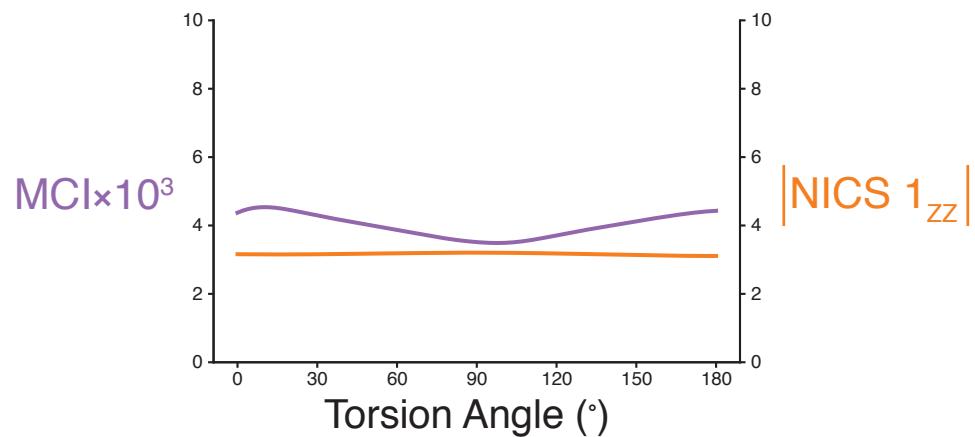


Figure B.5: Comparison of the aromaticity indexes MCI and NICS for hBT.

F2-BT

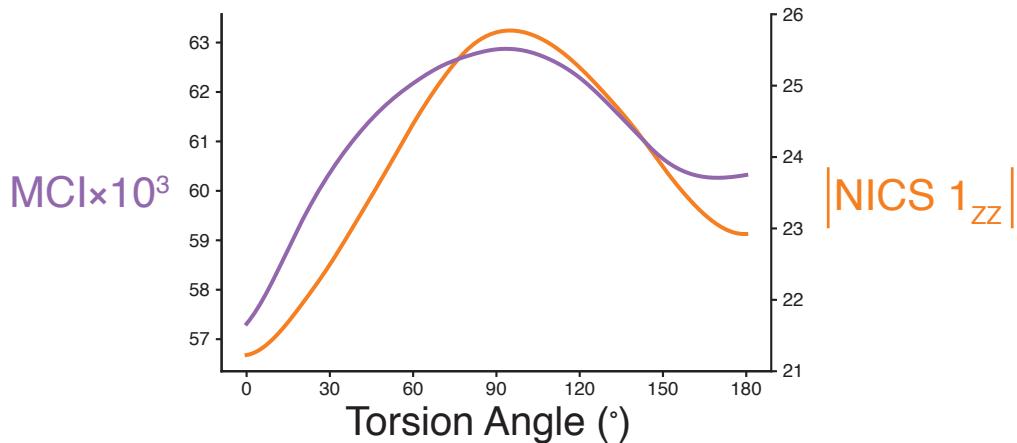


Figure B.6: Comparison of the aromaticity indexes MCI and NICS for F2-BT.

BEDOT

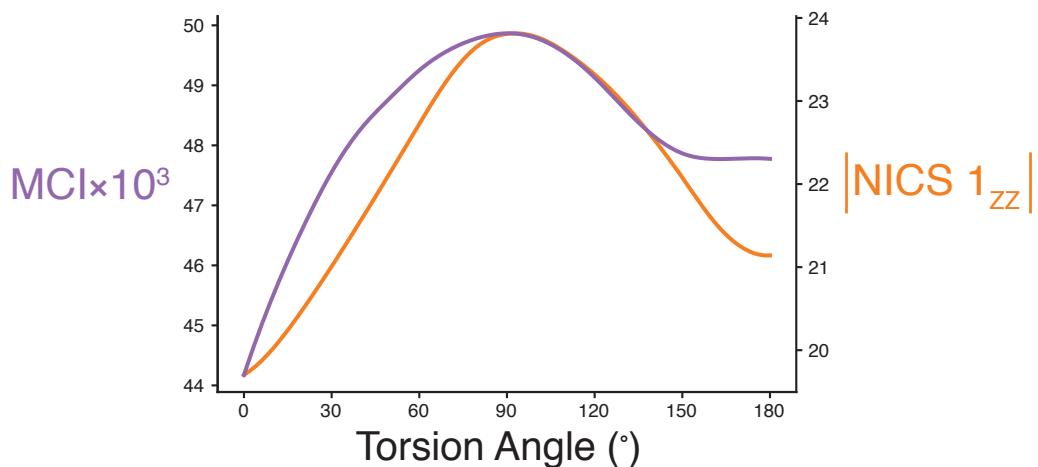


Figure B.7: Comparison of the aromaticity indexes MCI and NICS for BEDOT.

B.3 Through-space Calculations

$\text{H} \cdots \text{S}$

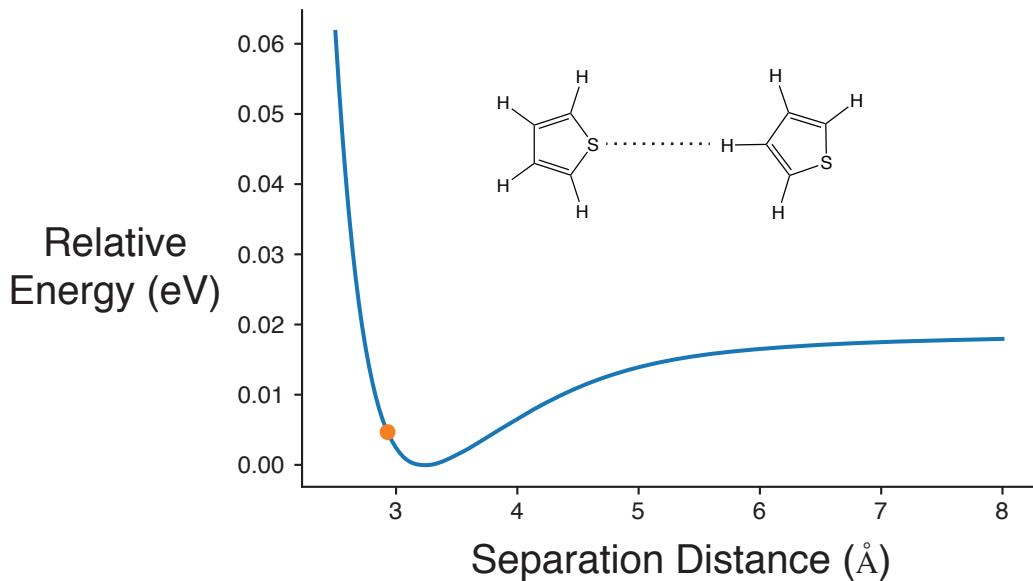


Figure B.8: A potential energy scan of the interatomic separation distance between a hydrogen and a sulfur atom on thiophene molecules. The orange dot represents the relaxed $\text{H} \cdots \text{S}$ distance on a trans (180°) BT molecule. This indicates that the $\text{H} \cdots \text{S}$ through-space interaction is marginally repulsive in trans BT. It is noteworthy that the repulsive energy is small compared to the torsional barrier present at 180° in BT (a factor of ~ 2.5), which in combination with the NCI analysis below demonstrate the minor role of sterics in determining planarity.

H \cdots S Noncovalent Interaction Analysis

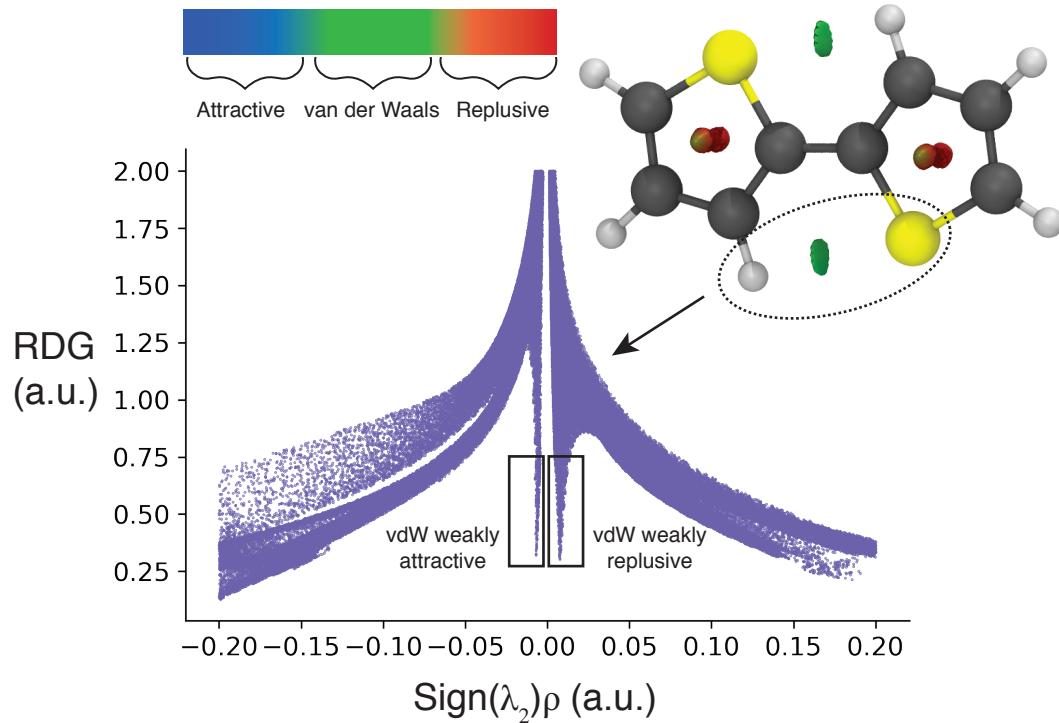


Figure B.9: The NCI analysis of BT including an NCI isosurface (right) and an $s(\rho)$ plot (center), which displays the reduced density gradient (RDG) as a function of the sign of the electron-density Hessian matrix's second eigenvalue ($\text{sign}(\lambda_2)$) times the electron-density (ρ). The isosurface plot on right shows a van der Waals interaction between H \cdots S. The color gradient at the top gives a rough physical description of the color scheme used for the isosurface. When only the localized region around H \cdots S is considered, by employing a radius cutoff, the $s(\rho)$ plot is inconclusive exhibiting both weakly repulsive and weakly attractive interactions.

F ... S

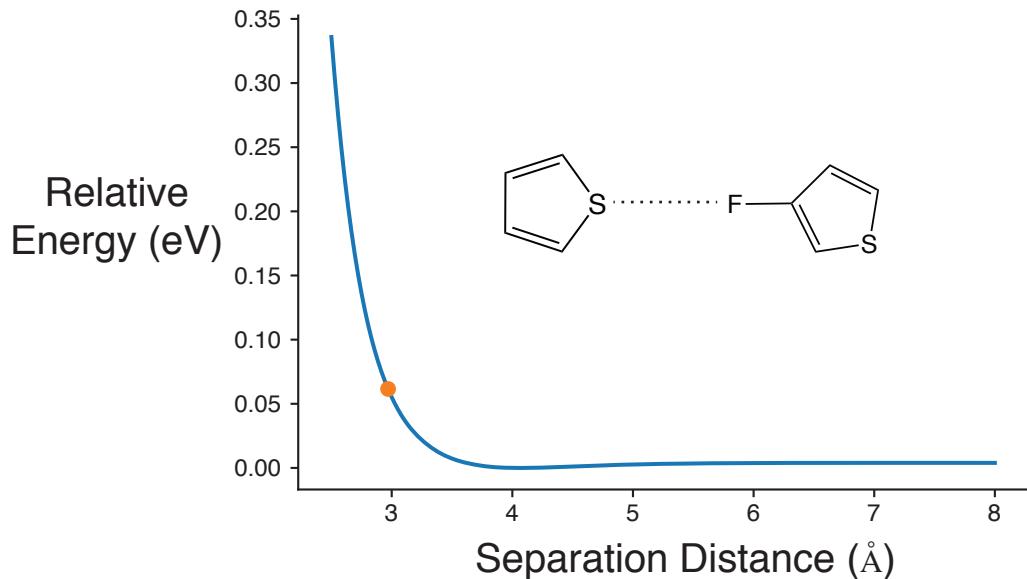


Figure B.10: A potential energy scan of the interatomic separation distance between a fluoride and a sulfur atom on a fluorinated thiophene and a thiophene molecule. The orange dot represents the relaxed $\text{F} \cdots \text{S}$ distance on a trans (180°) 3F-BT molecule. This indicates that the $\text{F} \cdots \text{S}$ through-space interaction is repulsive in trans 3F-BT.

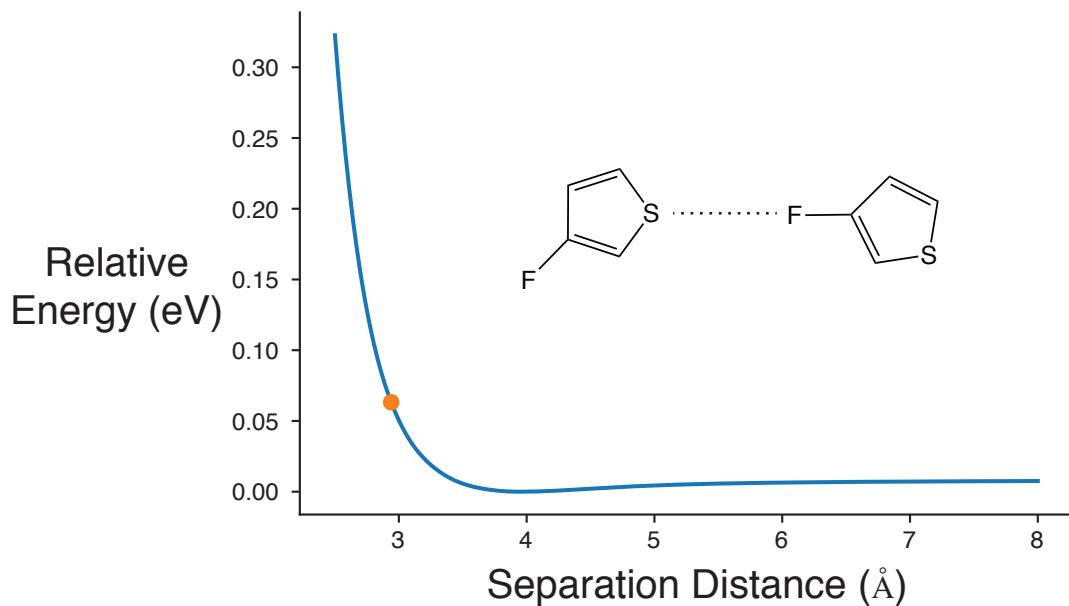


Figure B.11: A potential energy scan of the interatomic separation distance between a fluoride and a sulfur atom on a fluorinated thiophene molecules. The orange dot represents the relaxed $\text{F} \cdots \text{S}$ distance on a trans (180°) $\text{F}_2\text{-BT}$ molecule. This indicates that the $\text{F} \cdots \text{S}$ through-space interaction is repulsive in trans $\text{F}_2\text{-BT}$.

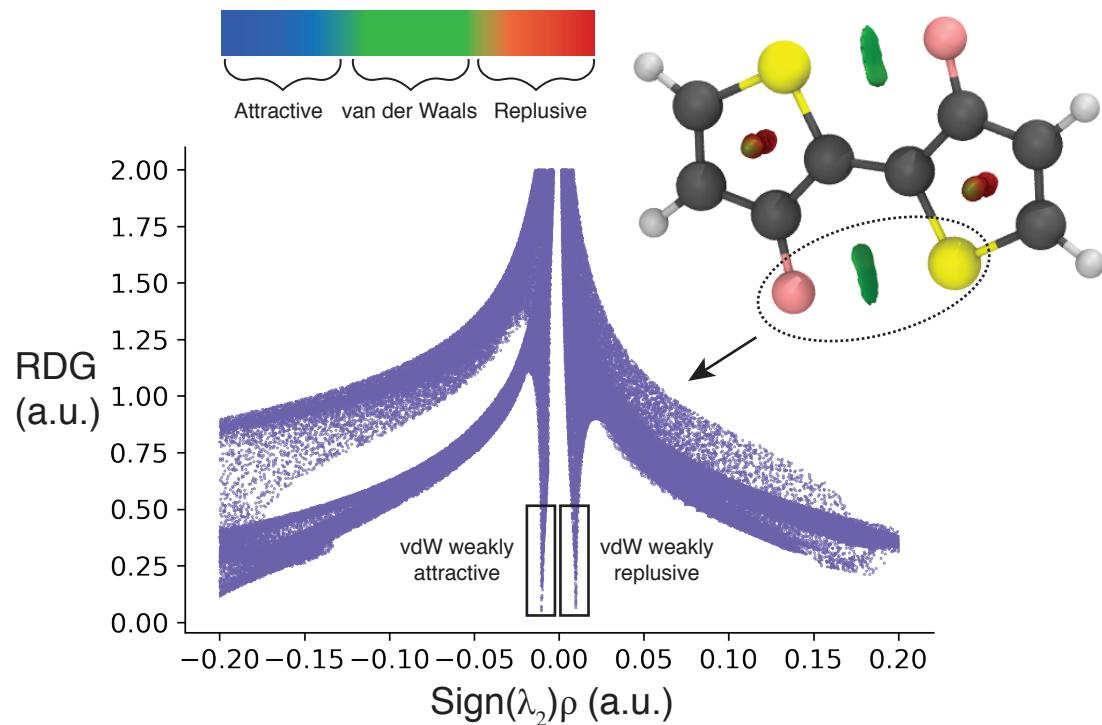
F . . . S Noncovalent Interaction Analysis


Figure B.12: The NCI analysis of F2-BT including an NCI isosurface (right) and an $s(\rho)$ plot (center), which displays the reduced density gradient (RDG) as a function of the sign of the electron-density Hessian matrix's second eigenvalue ($\text{sign}(\lambda_2)$) times the electron-density (ρ). The isosurface plot on right shows a van der Waals interaction between $\text{H} \cdots \text{S}$. The color gradient at the top gives a rough physical description of the color scheme used for the isosurface. When only the localized region around $\text{H} \cdots \text{S}$ is considered, by employing a radius cutoff, the $s(\rho)$ plot is inconclusive exhibiting both weakly repulsive and weakly attractive interactions.

O ... S

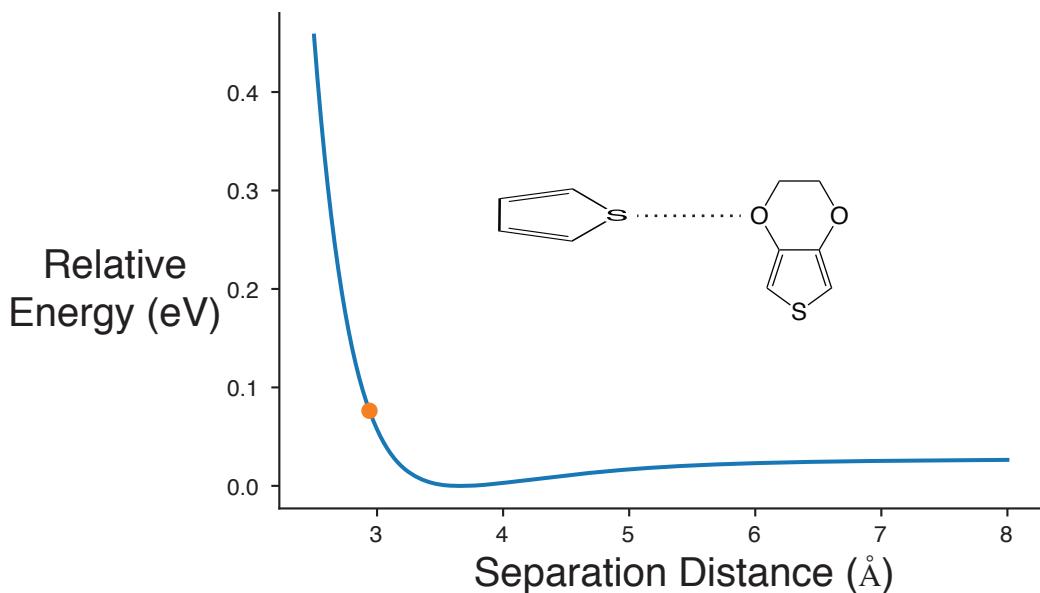


Figure B.13: A potential energy scan of the interatomic separation distance between a oxygen and a sulfur atom on an EDOT and thiophene molecule respectively. The thiophene molecule has been rotated such that the ring is perpendicular to the EDOT, this is done to minimize secondary H ... S interactions. The orange dot represents the relaxed O ... S distance on a trans (180°) BEDOT molecule. This indicates that the O ... S through-space interaction is repulsive in trans BEDOT.

O ... S Noncovalent Interaction Analysis

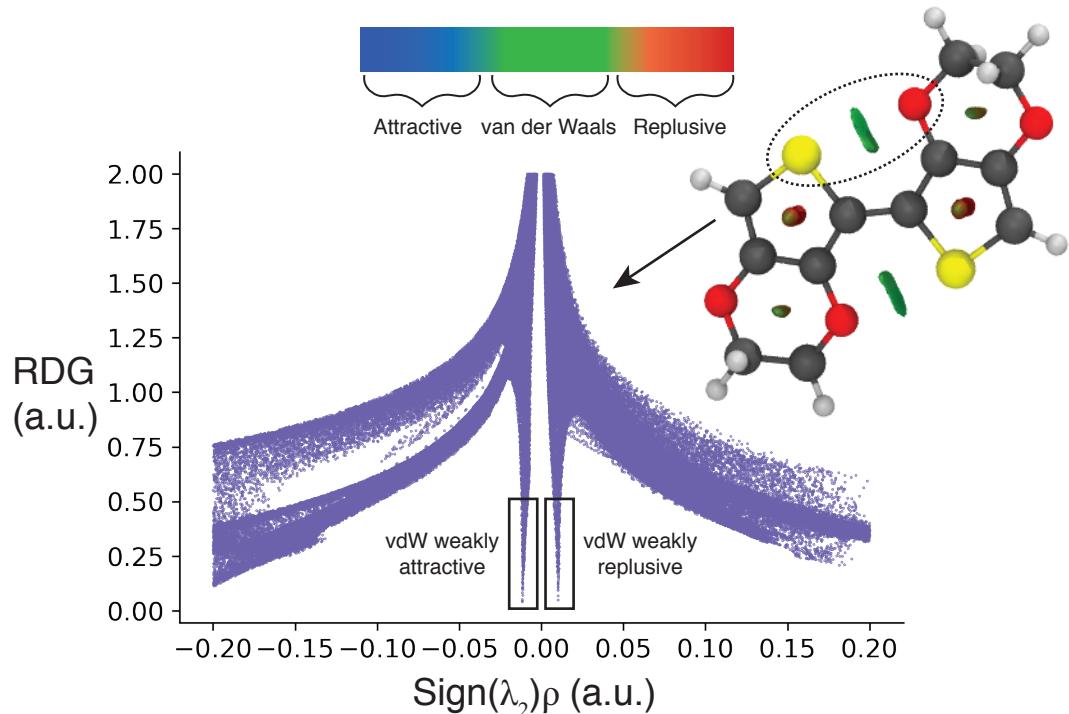


Figure B.14: The NCI analysis of BEDOT including an NCI isosurface (right) and an $s(\rho)$ plot (center), which displays the reduced density gradient (RDG) as a function of the sign of the electron-density Hessian matrix's second eigenvalue ($\text{sign}(\lambda_2)$) times the electron-density (ρ). The isosurface plot on right shows a van der Waals interaction between $\text{H} \cdots \text{S}$. The color gradient at the top gives a rough physical description of the color scheme used for the isosurface. When only the localized region around $\text{H} \cdots \text{S}$ is considered, by employing a radius cutoff, the $s(\rho)$ plot is inconclusive exhibiting both weakly repulsive and weakly attractive interactions.

B.4 NBO Perturbation Analysis

Table B.1: NBO Stabilization Energies

Donor	Acceptor	Stabilization Energy E(2) kcal/mol
F2-BT [†]	LP_F	σ_{C-S}^*
BEDOT [†]	LP_O	σ_{C-S}^*

[†] Energy values represent 180° configurations

B.5 Expanded Methods

Hydrogenation of BT

Additional torsional constraints were placed on the hBT dimer during geometry optimizations to prevent ring distortion. The intent of hydrogenation was to remove aromaticity, while maintaining conjugation across the central C-C bond between rings. Ring distortion is an unintended consequence of hydrogenation and does not represent the physics of interest. As a result, the intra-ring C-C-C-C torsion angle for each thiophene ring was fixed at its undistorted state (roughly 0°), in addition to the central inter-ring C-C-C-C torsion angle being fixed at the desired angle within the potential energy scan. In sum, geometry optimizations for the hBT dimer had 3 torsional constraints, 2 intra-ring and 1 inter-ring, whereas all other degrees of freedom were allowed to relax.

NICS Calculations

NICS values were computed by placing fictitious hydrogen atoms (designated H-Bq in Gaussian) 1Å above the center of each ring, followed by an NMR calculation with Gaussian16.[31] The largest eigenvalue of the magnetic shielding tensor for the fictitious H atom was taken as the NICS 1_{ZZ} value in ppm. Conventionally, the sign of NICS values are reversed for comparison with experimental NMR values. In this work we do not reverse the sign and report the absolute NICS 1_{ZZ} value ($|NICS1_{ZZ}|$) for easy comparison with MCI aromaticity values. Specific details on the NICS method have been described elsewhere.[26, 14]

Through-space Calculations

All through-space potential energy scans utilized counterpoise corrected energies as implementation in Gaussian16. Methodology of through-space calculations has been described by

others.[43]

NCI Analysis

NCI analysis was preformed with NCIplot.[46, 21] The only deviation from standard procedure was adding a radius cutoff to investigate local interactions (i.e. X ··· S). For these calculations a point was specified roughly half way between the two atoms with a radius cutoff of 2Å.

B.6 Tabular Data

BT

Table B.2: Bithiophene Torsional Data

Torsion Angle (°)	Rel. Energy (eV)	Abs. Energy (Hartree)	MCI $\times 10^3$ [†]	$ NICS ^{1zz}$ [‡]	Central Bond Length (Å)
0.0	0.04106	-1104.84898	66.19 (66.18)	24.24 (24.24)	1.455
10.0	0.03557	-1104.84919	66.30 (66.32)	24.53 (24.50)	1.455
20.0	0.02465	-1104.84959	66.69 (66.67)	25.15 (25.14)	1.454
30.0	0.01742	-1104.84985	67.25 (67.25)	25.85 (25.84)	1.455
40.0	0.01849	-1104.84981	67.96 (67.98)	26.48 (26.48)	1.456
50.0	0.02854	-1104.84944	68.83 (68.82)	27.03 (27.04)	1.458
60.0	0.04480	-1104.84885	69.83 (69.82)	27.48 (27.48)	1.460
70.0	0.06250	-1104.84820	70.80 (70.77)	27.83 (27.82)	1.463
80.0	0.07593	-1104.84770	71.54 (71.53)	28.09 (28.08)	1.465
90.0	0.07962	-1104.84757	71.88 (71.87)	28.25 (28.26)	1.466
100.0	0.07169	-1104.84786	71.60 (71.60)	28.27 (28.28)	1.465
110.0	0.05443	-1104.84849	70.81 (70.83)	28.08 (28.09)	1.463
120.0	0.03391	-1104.84925	69.80 (69.79)	27.70 (27.72)	1.460
130.0	0.01566	-1104.84992	68.71 (68.72)	27.14 (27.16)	1.458
140.0	0.00386	-1104.85035	67.71 (67.71)	26.44 (26.45)	1.456
150.0	0.00000	-1104.85049	66.82 (66.82)	25.64 (25.66)	1.454
160.0	0.00284	-1104.85039	66.12 (66.11)	24.82 (24.83)	1.454
170.0	0.00864	-1104.85018	65.61 (65.60)	24.15 (24.15)	1.454
180.0	0.01147	-1104.85007	65.42 (65.43)	23.88 (23.88)	1.454

^{*} All quantum calculations employed the ω B97x-D functional with the def2-TZVPP basis set.[†] The MCI values in parentheses represent the second ring in the dimer molecule.[‡] The units of NICS values are ppm, and for comparison with MCI we have not reversed the sign. The NICS values in parentheses represent the second ring in the dimer molecule.

Table B.3: Bithiophene Relaxed Structure

	Atom	x (Å)	y (Å)	z (Å)
1	S	0.001	-0.024	-0.030
2	C	1.708	-0.014	-0.014
3	H	2.244	-0.025	0.920
4	C	2.219	0.008	-1.274
5	H	3.277	0.017	-1.488
6	C	1.210	0.029	-2.269
7	H	1.409	0.069	-3.330
8	C	-0.054	0.021	-1.750
9	C	-1.326	0.042	-2.457
10	C	-2.520	0.567	-2.048
11	H	-2.646	1.070	-1.100
12	C	-3.553	0.408	-3.004
13	H	-4.563	0.763	-2.865
14	C	-3.130	-0.234	-4.126
15	H	-3.701	-0.478	-5.006
16	S	-1.481	-0.662	-4.020

* Level of theory: ω B97x-D
Basis set: def2-TZVPP

hBT

Table B.4: Hydrogenated Bithiophene Torsional Data

Torsion Angle (°)	Rel. Energy (eV)	Abs. Energy (Hartree)	MCI $\times 10^3$ [†]	$ ^{NICS}_{^{1ZZ}} $ [‡]	Central Bond Length (Å)
0.0	0.16920	-1107.25114	3.16 (3.16)	4.38 (4.37)	1.468
10.0	0.15361	-1107.25172	3.15 (3.15)	4.53 (4.54)	1.467
20.0	0.12613	-1107.25273	3.15 (3.15)	4.45 (4.45)	1.465
30.0	0.10310	-1107.25357	3.16 (3.16)	4.30 (4.29)	1.463
40.0	0.09123	-1107.25401	3.17 (3.17)	4.15 (4.15)	1.462
50.0	0.09212	-1107.25398	3.18 (3.18)	4.01 (4.01)	1.463
60.0	0.10437	-1107.25353	3.19 (3.19)	3.88 (3.87)	1.464
70.0	0.12360	-1107.25282	3.20 (3.20)	3.74 (3.73)	1.466
80.0	0.14340	-1107.25209	3.20 (3.20)	3.62 (3.60)	1.469
90.0	0.15647	-1107.25161	3.21 (3.21)	3.53 (3.51)	1.471
100.0	0.15718	-1107.25158	3.20 (3.20)	3.51 (3.49)	1.472
110.0	0.14297	-1107.25211	3.19 (3.19)	3.59 (3.57)	1.471
120.0	0.11631	-1107.25309	3.18 (3.18)	3.72 (3.71)	1.469
130.0	0.08418	-1107.25427	3.16 (3.16)	3.86 (3.86)	1.465
140.0	0.05374	-1107.25539	3.15 (3.15)	4.00 (3.99)	1.462
150.0	0.02927	-1107.25629	3.13 (3.13)	4.13 (4.12)	1.459
160.0	0.01226	-1107.25691	3.12 (3.12)	4.25 (4.25)	1.457
170.0	0.00288	-1107.25725	3.11 (3.11)	4.37 (4.36)	1.456
180.0	0.00000	-1107.25736	3.11 (3.11)	4.43 (4.43)	1.455

* All quantum calculations employed the ω B97x-D functional with the def2-TZVPP basis set.

† The MCI values in parentheses represent the second ring in the dimer molecule.

‡ The units of NICS values are ppm, and for comparison with MCI we have not reversed the sign. The NICS values in parentheses represent the second ring in the dimer molecule.

Table B.5: Hydrogenated Bithiophene Relaxed Structure

	Atom	x (Å)	y (Å)	z (Å)
1	S	-0.040	0.163	0.023
2	C	1.764	0.408	-0.006
3	C	2.271	-0.288	-1.271
4	C	1.149	-0.217	-2.264
5	H	1.308	-0.366	-3.324
6	C	-0.061	-0.024	-1.739
7	C	-1.330	-0.001	-2.449
8	C	-2.521	0.341	-1.955
9	H	-2.656	0.665	-0.932
10	C	-3.675	0.172	-2.898
11	C	-3.075	0.163	-4.306
12	S	-1.396	-0.522	-4.142
13	H	3.183	0.186	-1.635
14	H	2.513	-1.337	-1.068
15	H	1.963	1.478	-0.047
16	H	2.193	0.003	0.906
17	H	-3.641	-0.444	-5.008
18	H	-2.994	1.176	-4.699
19	H	-4.185	-0.774	-2.686
20	H	-4.417	0.965	-2.798

* Level of theory: ω B97x-D
 Basis set: def2-TZVPP

F2-BT

Table B.6: F2-BT Torsional Data

Torsion Angle (°)	Rel. Energy (eV)	Abs. Energy (Hartree)	MCI $\times 10^3$ [†]	$ NICS ^{1zz}$ [‡]	Central Bond Length (Å)
0.0	0.13549	-1303.34351	56.68 (56.66)	21.67 (21.66)	1.455
10.0	0.11315	-1303.34433	57.03 (57.03)	22.31 (22.31)	1.453
20.0	0.07472	-1303.34574	57.71 (57.73)	23.11 (23.11)	1.452
30.0	0.04179	-1303.34695	58.51 (58.51)	23.78 (23.78)	1.451
40.0	0.02160	-1303.34770	59.43 (59.43)	24.31 (24.31)	1.451
50.0	0.01574	-1303.34791	60.37 (60.36)	24.72 (24.72)	1.452
60.0	0.02076	-1303.34773	61.36 (61.35)	25.03 (25.03)	1.454
70.0	0.03013	-1303.34738	62.22 (62.23)	25.27 (25.27)	1.456
80.0	0.03786	-1303.34710	62.88 (62.88)	25.42 (25.42)	1.457
90.0	0.04052	-1303.34700	63.21 (63.21)	25.51 (25.51)	1.458
100.0	0.03844	-1303.34708	63.21 (63.20)	25.49 (25.49)	1.458
110.0	0.03382	-1303.34725	62.95 (62.95)	25.35 (25.35)	1.457
120.0	0.02904	-1303.34742	62.50 (62.49)	25.11 (25.11)	1.455
130.0	0.02505	-1303.34757	61.91 (61.92)	24.75 (24.75)	1.454
140.0	0.02163	-1303.34769	61.25 (61.24)	24.35 (24.35)	1.453
150.0	0.01725	-1303.34786	60.48 (60.48)	23.98 (23.98)	1.451
160.0	0.01002	-1303.34812	59.80 (59.80)	23.76 (23.76)	1.450
170.0	0.00297	-1303.34838	59.30 (59.29)	23.71 (23.71)	1.449
180.0	0.00000	-1303.34849	59.13 (59.13)	23.75 (23.75)	1.449

* All quantum calculations employed the ω B97x-D functional with the def2-TZVPP basis set.

† The MCI values in parentheses represent the second ring in the dimer molecule.

‡ The units of NICS values are ppm, and for comparison with MCI we have not reversed the sign. The NICS values in parentheses represent the second ring in the dimer molecule.

Table B.7: F2-BT Relaxed Structure

	Atom	x (Å)	y (Å)	z (Å)
1	S	0.037	-0.486	-0.078
2	C	1.727	-0.266	-0.036
3	H	2.270	-0.443	0.877
4	C	2.227	0.132	-1.235
5	H	3.265	0.332	-1.445
6	C	1.196	0.254	-2.189
7	F	1.446	0.634	-3.445
8	C	-0.062	-0.040	-1.745
9	C	-1.307	-0.007	-2.484
10	C	-2.565	-0.304	-2.040
11	F	-2.815	-0.686	-0.785
12	C	-3.596	-0.181	-2.994
13	H	-4.634	-0.382	-2.784
14	C	-3.097	0.220	-4.192
15	H	-3.639	0.399	-5.105
16	S	-1.406	0.441	-4.150

* Level of theory: ω B97x-D
 Basis set: def2-TZVPP

Table B.8: F2-BT RHF and RHF NBO Deletion Energies

Torsion Angle (°)	RHF		RHF Deletion [†]	
	Rel. Energy (eV)	Abs. Energy (Hartree)	Rel. Energy (eV)	Abs. Energy (Hartree)
0.0	0.13996	-1299.37850	0.16754	-1299.35295
10.0	0.11538	-1299.37940	0.13726	-1299.35406
20.0	0.07148	-1299.38101	0.08629	-1299.35593
30.0	0.03270	-1299.38244	0.04196	-1299.35756
40.0	0.00841	-1299.38333	0.01336	-1299.35861
50.0	0.00000	-1299.38364	0.00116	-1299.35906
60.0	0.00259	-1299.38354	0.00000	-1299.35910
70.0	0.00899	-1299.38331	0.00320	-1299.35899
80.0	0.01411	-1299.38312	0.00638	-1299.35887
90.0	0.01607	-1299.38305	0.00783	-1299.35882
100.0	0.01536	-1299.38307	0.00735	-1299.35883
110.0	0.01359	-1299.38314	0.00606	-1299.35888
120.0	0.01250	-1299.38318	0.00567	-1299.35890
130.0	0.01301	-1299.38316	0.00796	-1299.35881
140.0	0.01444	-1299.38311	0.01437	-1299.35858
150.0	0.01453	-1299.38311	0.02579	-1299.35816
160.0	0.01131	-1299.38322	0.04070	-1299.35761
170.0	0.00639	-1299.38340	0.05317	-1299.35715
180.0	0.00405	-1299.38349	0.05803	-1299.35697

^{*} All quantum calculations employed the restricted Hartree-Fock (RHF) level of theory with the def2-TZVPP basis set.[†] NBO6 and Gaussian09 were used to delete both σ_{C-S}^* orbitals from the Fock matrix and calculate the corresponding energy.

BEDOT

Table B.9: BEDOT Torsional Data

Torsion Angle (°)	Rel. Energy (eV)	Abs. Energy (Hartree)	MCI $\times 10^3$ [†]	$ NICS ^{‡}$	Central Bond Length (Å)
0.0	0.22303	-1560.56546	44.17 (44.18)	19.73 (19.70)	1.457
10.0	0.18094	-1560.56701	44.62 (44.61)	20.68 (20.66)	1.453
20.0	0.12507	-1560.56906	45.26 (45.24)	21.50 (21.46)	1.451
30.0	0.07837	-1560.57078	45.98 (45.97)	22.15 (22.14)	1.450
40.0	0.04952	-1560.57184	46.75 (46.75)	22.65 (22.66)	1.450
50.0	0.04054	-1560.57217	47.54 (47.57)	23.04 (23.04)	1.451
60.0	0.04721	-1560.57192	48.36 (48.35)	23.36 (23.37)	1.453
70.0	0.06129	-1560.57140	49.12 (49.13)	23.59 (23.61)	1.455
80.0	0.07344	-1560.57096	49.66 (49.66)	23.74 (23.76)	1.457
90.0	0.07919	-1560.57075	49.86 (49.87)	23.80 (23.82)	1.457
100.0	0.07864	-1560.57077	49.81 (49.82)	23.74 (23.76)	1.457
110.0	0.07479	-1560.57091	49.55 (49.55)	23.56 (23.57)	1.456
120.0	0.06940	-1560.57111	49.18 (49.18)	23.28 (23.28)	1.455
130.0	0.06277	-1560.57135	48.70 (48.71)	22.92 (22.92)	1.453
140.0	0.05341	-1560.57169	48.12 (48.15)	22.57 (22.58)	1.452
150.0	0.03956	-1560.57220	47.46 (47.47)	22.36 (22.37)	1.450
160.0	0.02210	-1560.57284	46.78 (46.78)	22.30 (22.30)	1.448
170.0	0.00637	-1560.57342	46.31 (46.33)	22.31 (22.31)	1.447
180.0	0.00000	-1560.57366	46.17 (46.16)	22.31 (22.30)	1.447

* All quantum calculations employed the ω B97x-D functional with the def2-TZVPP basis set.

† The MCI values in parentheses represent the second ring in the dimer molecule.

‡ The units of NICS values are ppm, and for comparison with MCI we have not reversed the sign. The NICS values in parentheses represent the second ring in the dimer molecule.

Table B.10: BEDOT Relaxed Structure

	Atom	x (Å)	y (Å)	z (Å)
1	S	0.212	-0.710	-0.167
2	C	1.900	-0.439	-0.177
3	H	2.495	-0.581	0.709
4	C	2.326	-0.036	-1.400
5	C	1.269	0.050	-2.346
6	C	0.043	-0.282	-1.835
7	C	-1.226	-0.307	-2.529
8	C	-2.452	-0.637	-2.018
9	C	-3.507	-0.570	-2.969
10	C	-3.076	-0.196	-4.200
11	H	-3.668	-0.069	-5.090
12	S	-1.389	0.082	-4.208
13	O	3.615	0.245	-1.723
14	O	1.472	0.443	-3.630
15	C	3.723	0.974	-2.936
16	C	2.838	0.375	-4.009
17	H	4.768	0.928	-3.234
18	H	3.445	2.019	-2.765
19	H	2.930	0.933	-4.938
20	H	3.118	-0.668	-4.187
21	O	-4.792	-0.873	-2.652
22	O	-2.663	-0.982	-0.722
23	C	-5.017	-0.878	-1.251
24	C	-3.915	-1.622	-0.527
25	H	-4.096	-1.629	0.545
26	H	-3.859	-2.654	-0.889
27	H	-5.976	-1.366	-1.092
28	H	-5.074	0.152	-0.883

* Level of theory: ω B97x-D
 Basis set: def2-TZVPP

Table B.11: BEDOT RHF and RHF NBO Deletion Energies

Torsion Angle (°)	RHF		RHF Deletion [†]	
	Rel. Energy (eV)	Abs. Energy (Hartree)	Rel. Energy (eV)	Abs. Energy (Hartree)
0.0	0.24056	-1554.97676	0.27723	-1554.95816
10.0	0.19528	-1554.97842	0.21892	-1554.96030
20.0	0.12939	-1554.98084	0.14046	-1554.96319
30.0	0.07253	-1554.98293	0.07378	-1554.96564
40.0	0.03418	-1554.98434	0.02806	-1554.96732
50.0	0.01693	-1554.98497	0.00498	-1554.96817
60.0	0.01697	-1554.98497	0.00000	-1554.96835
70.0	0.02545	-1554.98466	0.00418	-1554.96819
80.0	0.03364	-1554.98436	0.00935	-1554.96800
90.0	0.03754	-1554.98422	0.01187	-1554.96791
100.0	0.03768	-1554.98421	0.01140	-1554.96793
110.0	0.03625	-1554.98426	0.00965	-1554.96799
120.0	0.03520	-1554.98430	0.00867	-1554.96803
130.0	0.03508	-1554.98431	0.01027	-1554.96797
140.0	0.03436	-1554.98433	0.01590	-1554.96776
150.0	0.02949	-1554.98451	0.02701	-1554.96736
160.0	0.01838	-1554.98492	0.04181	-1554.96681
170.0	0.00578	-1554.98538	0.05353	-1554.96638
180.0	0.00000	-1554.98560	0.05803	-1554.96622

* All quantum calculations employed the restricted Hartree-Fock (RHF) level of theory with the def2-TZVPP basis set.

† NBO6 and Gaussian09 were used to delete both σ_{C-S}^* orbitals from the Fock matrix and calculate the corresponding energy.

3F-BT

Table B.12: 3F-BT Torsional Data

Torsion Angle (°)	Rel. Energy (eV)	Abs. Energy (Hartree)	MCI $\times 10^3$ [†]	$ NICS ^{‡}$	Central Bond Length (Å)
0.0	0.00895	-1204.09895	58.05 (64.89)	22.05 (24.75)	1.452
10.0	0.00627	-1204.09905	58.21 (65.11)	22.47 (24.98)	1.452
20.0	0.00159	-1204.09922	58.69 (65.67)	23.15 (25.49)	1.452
30.0	0.00000	-1204.09928	59.28 (66.51)	23.81 (26.05)	1.452
40.0	0.00442	-1204.09912	60.04 (67.49)	24.39 (26.57)	1.454
50.0	0.01515	-1204.09872	60.85 (68.62)	24.84 (27.03)	1.455
60.0	0.02952	-1204.09820	61.64 (69.80)	25.17 (27.43)	1.458
70.0	0.04379	-1204.09767	62.38 (70.90)	25.41 (27.74)	1.460
80.0	0.05374	-1204.09731	62.92 (71.75)	25.58 (27.99)	1.462
90.0	0.05643	-1204.09721	63.12 (72.18)	25.67 (28.15)	1.462
100.0	0.05146	-1204.09739	62.95 (72.13)	25.67 (28.16)	1.462
110.0	0.04101	-1204.09777	62.45 (71.66)	25.51 (28.01)	1.460
120.0	0.02875	-1204.09822	61.72 (70.96)	25.16 (27.76)	1.458
130.0	0.01745	-1204.09864	60.86 (70.08)	24.62 (27.41)	1.456
140.0	0.00919	-1204.09894	59.93 (69.22)	23.88 (27.04)	1.454
150.0	0.00454	-1204.09911	59.03 (68.39)	23.05 (26.67)	1.453
160.0	0.00247	-1204.09919	58.25 (67.69)	22.24 (26.36)	1.452
170.0	0.00173	-1204.09922	57.69 (67.21)	21.73 (26.11)	1.451
180.0	0.00170	-1204.09922	57.49 (67.05)	21.67 (25.92)	1.451

* All quantum calculations employed the ω B97x-D functional with the def2-TZVPP basis set.

† The MCI values in parentheses represent the second ring in the dimer molecule.

‡ The units of NICS values are ppm, and for comparison with MCI we have not reversed the sign. The NICS values in parentheses represent the second ring in the dimer molecule.

Table B.13: 3F-BT Relaxed Structure

	Atom	x (Å)	y (Å)	z (Å)
1	S	0.027	-0.481	-0.106
2	C	1.720	-0.267	-0.041
3	H	2.251	-0.447	0.878
4	C	2.229	0.132	-1.234
5	H	3.271	0.330	-1.433
6	C	1.208	0.259	-2.201
7	F	1.475	0.640	-3.452
8	C	-0.054	-0.033	-1.770
9	C	-1.311	-0.006	-2.495
10	C	-2.555	-0.315	-2.013
11	H	-2.733	-0.626	-0.994
12	C	-3.576	-0.186	-2.983
13	H	-4.619	-0.385	-2.790
14	C	-3.097	0.220	-4.189
15	H	-3.648	0.398	-5.097
16	S	-1.407	0.446	-4.157

* Level of theory: ω B97x-D
 Basis set: def2-TZVPP

4F-BT

Table B.14: 4F-BT Torsional Data

Torsion Angle (°)	Rel. Energy (eV)	Abs. Energy (Hartree)	MCI $\times 10^3$ [†]	$ NICS ^{‡}$	Central Bond Length (Å)
0.0	0.04013	-1204.09890	57.89 (66.42)	21.76 (24.38)	1.454
10.0	0.03445	-1204.09911	58.02 (66.56)	22.05 (24.67)	1.454
20.0	0.02336	-1204.09952	58.38 (66.91)	22.68 (25.35)	1.454
30.0	0.01622	-1204.09978	58.90 (67.43)	23.38 (26.04)	1.454
40.0	0.01770	-1204.09973	59.60 (68.15)	24.03 (26.68)	1.455
50.0	0.02851	-1204.09933	60.43 (68.98)	24.59 (27.20)	1.457
60.0	0.04586	-1204.09869	61.39 (69.95)	25.03 (27.60)	1.460
70.0	0.06472	-1204.09800	62.33 (70.90)	25.37 (27.90)	1.462
80.0	0.07900	-1204.09747	63.11 (71.66)	25.62 (28.11)	1.465
90.0	0.08278	-1204.09733	63.43 (71.94)	25.77 (28.25)	1.465
100.0	0.07420	-1204.09765	63.17 (71.66)	25.78 (28.26)	1.465
110.0	0.05592	-1204.09832	62.40 (70.86)	25.61 (28.09)	1.462
120.0	0.03445	-1204.09911	61.40 (69.87)	25.25 (27.76)	1.460
130.0	0.01557	-1204.09980	60.36 (68.85)	24.73 (27.26)	1.457
140.0	0.00357	-1204.10025	59.40 (67.90)	24.06 (26.62)	1.455
150.0	0.00000	-1204.10038	58.53 (67.12)	23.28 (25.90)	1.454
160.0	0.00354	-1204.10025	57.84 (66.48)	22.46 (25.10)	1.453
170.0	0.01018	-1204.10000	57.36 (66.03)	21.76 (24.44)	1.453
180.0	0.01340	-1204.09988	57.15 (65.87)	21.47 (24.15)	1.453

* All quantum calculations employed the ω B97x-D functional with the def2-TZVPP basis set.

† The MCI values in parentheses represent the second ring in the dimer molecule.

‡ The units of NICS values are ppm, and for comparison with MCI we have not reversed the sign. The NICS values in parentheses represent the second ring in the dimer molecule.

Table B.15: 4F-BT Relaxed Structure

	Atom	x (Å)	y (Å)	z (Å)
1	S	-0.024	-0.016	-0.026
2	C	1.685	-0.031	0.011
3	H	2.237	-0.073	0.933
4	C	2.172	0.019	-1.253
5	F	3.475	0.024	-1.537
6	C	1.192	0.056	-2.269
7	H	1.419	0.072	-3.324
8	C	-0.070	0.034	-1.746
9	C	-1.341	0.053	-2.452
10	C	-2.529	-0.510	-2.077
11	H	-2.647	-1.081	-1.167
12	C	-3.566	-0.292	-3.017
13	H	-4.572	-0.664	-2.901
14	C	-3.151	0.431	-4.092
15	H	-3.726	0.732	-4.951
16	S	-1.505	0.863	-3.962

* Level of theory: ω B97x-D
Basis set: def2-TZVPP