

Aromaticity as a Guide to Planarity in Conjugated Molecules and Polymers

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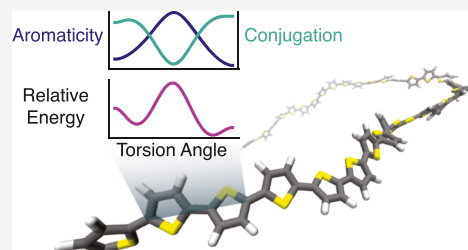
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ABSTRACT: Conjugated molecules and polymers have the ability to be transformative semiconducting materials; however, to reach their full potential a detailed understanding of the factors governing the molecular structure is crucial for establishing design principles for improved materials. Creating planar or “locking” structures is of particular interest for tuning electronic properties. While noncovalent locks are an effective strategy for increasing planarity, the precise interactions leading to these planar structures are often unknown or mischaracterized. In this study, we demonstrate that aromaticity can be used to investigate, interpret, and modify the complex physical interactions which lead to planarity. Furthermore, we clearly illustrate the important role aromaticity has in determining the structure through torsional preferences and find that modern noncovalent locks utilize hyperconjugation to alter aromaticity and increase planarity. We envision that our approach and our explanation of prevalent noncovalent locks will assist in the design of improved materials for organic electronics.



INTRODUCTION

Organic semiconductors offer unique blends of physical and electronic properties along with the processability and fabrication potential of polymers and small molecules.^{1,2} This combination opens up countless opportunities for new functional materials that can be tailored for specific applications.^{3–6} One successful strategy for tuning molecular properties is adding pendant groups to the conjugated backbone; these “noncovalent locks” control the molecular structure by inducing nonbonded interactions.^{7–10} The goal is to create structures that prefer coplanar torsional configurations that maximize electron delocalization across the molecule or polymer (i.e., conjugation),¹¹ 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.⁷ 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^{12–18}—do not involve nontraditional hydrogen bonding. Conboy et al. confirmed the importance of heteroatom interactions in poly-EDOT and similar molecules but stated that a precise description of torsional energetics was unclear and speculated that electrostatics were responsible for the observed planarity.⁹

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^{10,19,20} influences planarity in organic electronic materials. We show that the introduction of popular noncovalent locks modifies aromaticity and drives structures toward planarity. Finally, we identify the specific hyperconjugation interaction that alters aromaticity and determines planarity.

RESULTS AND DISCUSSION

An illustrative example of the balance between ring aromaticity and conjugation is the torsion potential of bithiophene (BT) (Figure 1). Dimers provide a computationally efficient and accurate representation of the torsion potential and trends in aromaticity observed in larger conjugated polymers (see Supporting Information Section 1)²¹ and hence are used throughout this work. The aromaticity of individual rings is quantified using the MCI,^{22,23} and the nucleus-independent chemical shift (NICS)^{24,25} (see Supporting Information Section 2), with both methods producing very similar results. We represent conjugation semiquantitatively as the normalized relative bond length of the bridge C–C bond between rings;

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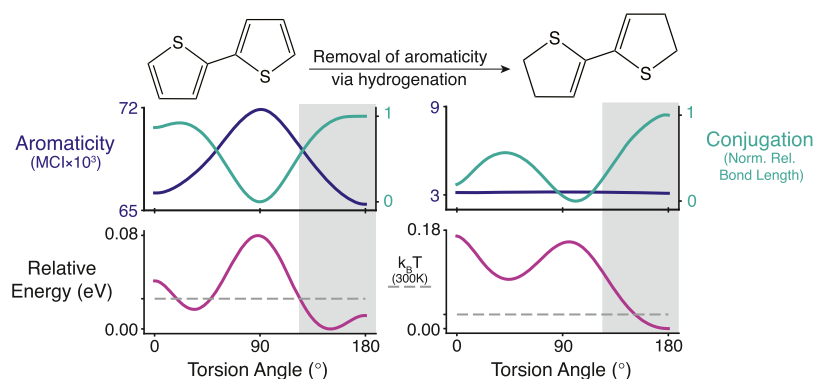


Figure 1. Ring aromaticity, molecular conjugation, and relative energies are plotted as a function of the torsion angle for BT and hBT. Both BT and hBT structures are represented in the 180° (trans) configuration. Aromaticity and conjugation are directly opposed in BT at 180° and the balance between the two driving forces results in a nonplanar torsional minimum around 150°. This key region is highlighted with gray shading. 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 × 10³) 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.

the rationale being configurations with shorter bridge bonds are more conjugated.^{26,27} 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. In contrast, 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 nonplanar global minimum at 150° in the torsion potential appears to reflect 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 Figure 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...S distance is reduced in hydrogenated BT (hBT) (2.78 Å in the 180° configuration) compared to BT (2.93 Å in the 180° configuration), which reduces concern that the 150° torsional minimum in BT is because of steric repulsion between H...S. This conclusion is supported with through-space calculations (Figure S8) and noncovalent interaction (NCI) analysis (Figure S12).^{28,29} 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 that a number of reported noncovalent locks modify aromaticity. As observed in the top of Figure 2 both 3,3'-difluorobithiophene (F2-BT) and bis-EDOT (BEDOT) exhibit a coplanar torsional minimum at 180° accompanied by a reduction in the aromaticity change between 90 and 180° compared to BT. As expected, conjugation is minimized at 90° and is maximized at 180°; it has been omitted from Figure 2 for clarity. For torsional energetics the magnitude of

aromaticity is less important 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 primarily interested in the change of aromaticity between 90 and 180° because they represent the extrema which generate the torsional driving force that has the largest influence on planarity.

To further investigate the modification of ring aromaticity and its impact on planarity we systematically added fluorine at different positions on one thiophene ring, termed ring 1, within the BT molecule (bottom of Figure 2) and examined the torsional dependence. We find that ring aromaticity is only altered in a manner that encourages planarity when the F atom is in position 3 near the S atom of the adjacent ring, which we denote as ring 2. The aromaticity of ring 1, where F is covalently bonded, is reduced by a constant across all torsion angles regardless of the F atom position. This is consistent with earlier reports that adding halogen substituents to an aromatic ring reduces the overall aromaticity.^{30,31} However, there remains a torsional driving force because of the constant reduction in the aromaticity of ring 1. Clearly, the F atom position is important, as 4F-BT retains a nonplanar energetic minimum around 150°, whereas 3F-BT has a planar minimum at 180°. Together these results indicate that there is an advantageous noncovalent inter-ring interaction between F...S causing a change in aromaticity and promoting planarity.

Using natural bonding orbital (NBO) analysis we identify the key interaction responsible for the modification of aromaticity and for stabilizing the planar 180° configuration (Figure 3). Our through-space calculations for F...S and O...S indicate that both would be repulsive at the respective relaxed separation distance present in the 180° configuration of F2-BT and BEDOT (see Supporting Information Section 3). Thus, it is clear that some other interaction involving X...S is stabilizing the repulsive effects in order for the 180° configuration to be energetically favorable. For both F2-BT and BEDOT, NBO perturbation analyses revealed a 3-center-2-electron interaction between a heteroatom lone pair (LP) and a C–S antibonding orbital (σ_{C-S}^*) pictured in the top of Figure 3. Details on stabilization energies are provided in Section 5 of the Supporting Information. Similar interactions have been

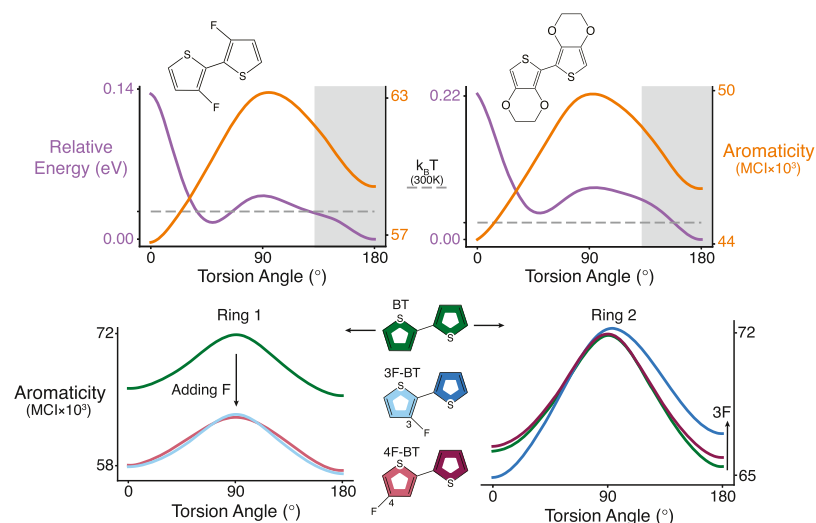


Figure 2. (Top) Torsional relative energies and aromaticity are plotted for F2-BT and BEDOT. In both systems, the change in aromaticity between 90 and 180° is reduced compared to BT and this corresponds to an energetic minimum near 180°. (Bottom) Ring 1 and ring 2 aromaticities are plotted against torsion angles for BT, 3F-BT, and 4F-BT. Both rings are plotted because 3F-BT and 4F-BT molecules are no longer symmetric. 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 altered near 180° similar to the plots in the top of the figure.

reported for the association of supramolecules.³² Conboy et al. mentioned this type of interaction as a possible source of attraction in BEDOT-like molecules, but dismissed it because of a lack of bond length correlations across a series of related molecules.⁹

In order to confirm the importance of the 3-center-2-electron interaction we utilized the NBO deletion method,³³ which has been used previously to deconvolute torsional energetics.³⁴ 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 F2-BT and BEDOT such that the planar 180° configurations are no longer favorable (as shown in Figure 3), most likely because of the 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.^{34,35} This result, which we found by observing changes in ring aromaticity, provides strong evidence that hyperconjugation is the critical interaction responsible for the locking behavior in these molecules and associated polymers.

CONCLUSIONS

Using a novel combination of quantum chemistry techniques, we have demonstrated the power of employing aromaticity as a guide to understanding the complex interactions that give rise to the atomic structure of conjugated molecules and polymers. In general, both aromaticity and conjugation are stabilizing and energetically favorable, yet we have shown that ring aromaticity favors torsioned or nonplanar configurations because it confines delocalized electrons within a ring instead of delocalizing them across the molecule or polymer as preferred by conjugation. We directly quantified the competition

between aromaticity and conjugation in an ideal BT system which results in a nonplanar minimum energy structure. Further, we found that the torsional driving force from aromaticity can indeed be beneficially altered through pendant group additions, such as those in state-of-the-art noncovalent locks F2-BT and BEDOT. To probe the exact nature of this interaction we identified and removed hyperconjugation between a heteroatom (i.e., F and O) LP and the C–S antibonding orbital on the adjacent ring, concluding that hyperconjugation is key for the changes in aromaticity and the resulting planarity, contrary to the previous work that suggested electrostatic interactions dominate. Our findings, therefore, indicate that aromaticity can serve as a new handle or screen for tuning the structure and the resulting electronic properties of conjugated materials. 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.

Computational Details. All quantum chemistry calculations were performed with Gaussian 16 unless otherwise noted.³⁶ The default level of theory was ω B97x-D with the def2-TZVPP basis set.^{37,38} 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 Supporting Information Subsection 6.1). 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.³⁹ NBO analysis was performed using NBO6.³³ All RHF and RHF NBO orbital deletions were done with Gaussian 09⁴⁰ 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

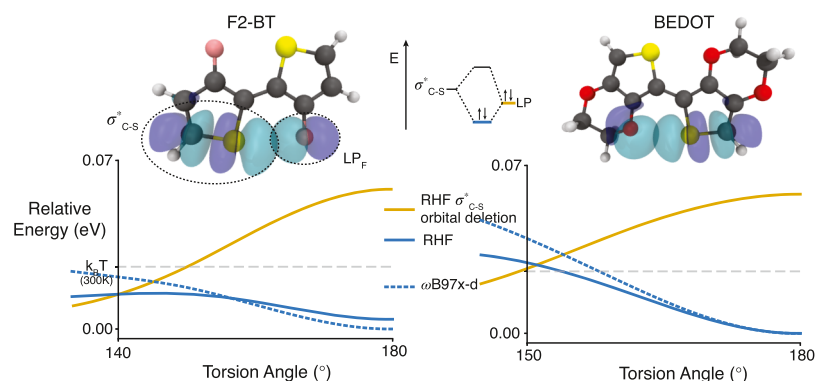


Figure 3. (Top) Isosurface plots of the overlap between C–S antibonding (σ^*_{C-S}) and F or O LP NBOs in F2-BT and BEDOT (isovalues ≈ 0.03). The orbital overlap leads to a stabilizing hyperconjugation interaction depicted in between the isosurface plots. (Bottom) The torsion potentials of F2-BT and 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.

with VMD,⁴¹ and all plotting utilized Matplotlib and cubic spline interpolation via SciPy.⁴²

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.0c01064>.

Examination of different length polymer chains; comparison of MCI and NICS aromaticity values; through-space calculations; NCI analysis; NBO perturbation analysis; and expanded methods (PDF)

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Notes

The authors declare no competing financial interest.

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