# Conformational Analysis of Conjugated Organic Materials: What Are My Heteroatoms Really Doing?

Karl J. Thorley*[1] and Christian B. Nielsen*[2]

1. Center for Applied Energy Research, University of Kentucky, Lexington KY 40511, USA; karl.thorley@uky.edu
2. Department of Chemistry, Queen Mary University of London, Mile End Road, London E1 4NS, UK; c.b.nielsen@qmul.ac.uk

## Abstract

Organic semiconductor small molecules and polymers often incorporate heteroatoms into their chemical structures to affect the electronic properties of the material. A particular design philosophy has been to use these heteroatoms to influence torsional potentials, since the overlap of adjacent π-orbitals is most efficient in planar systems and is critical for charge delocalization in these systems. Since these design rules became popular, the messages from the earlier works have become lost in a sea of reports of "conformational locks", where the non-covalent interactions have relatively small contributions to planarizing torsional potentials. Greater influences can be found in the stabilization by extended conjugation, consideration of steric repulsion, and the interactions involving solubilizing chains and neighboring molecules or polymer chains in condensed phases.

## 1. Introduction

The field of organic semiconductors (OSCs) based on singly bonded aromatic (hetero)cycles continues to develop new materials for applications in organic electronics, photovoltaics, electrochromics, bio-sensing and photocatalysis to name a few.[1,2] Since the advent of polythiophenes as OSC, such as the ubiquitous poly(3-hexylthiophene) (P3HT),[3] the presence of heteroatoms in the otherwise carbon-based framework[4,5] has been used to alter material properties, such as ionization potential or light absorption. These heteroatoms naturally alter charge distribution within the polymers or small molecules, cause polarization of the covalent bonds, and influence structural properties of the material through inter- and intra-chain non-covalent interactions.[6] It is perhaps the non-covalent interactions which have attracted the greatest attention in OSC molecular design,[7,8] many materials seemingly involving heteroatoms in the search of "conformational locks" and planarized conjugated systems.[8] But how great are these effects? This Perspective article highlights some of the aspects of introducing heteroatoms in organic semiconducting polymers and small molecules. Rather than providing a specific roadmap for materials design, we aim to emphasize that heteroatoms fulfil multiple roles which should all be considered during development of novel OSCs.

## 2. Currently Adopted Approaches

### 2.1. Torsional Potential Energy Surfaces (PES)

A common structural design of OSC materials is the connecting of repeat monomer units by a single covalent bond. This approach allows the synthesis of a wide range of polymers through transition metal catalyzed cross-coupling reactions, allowing a vast array of polymers and oligomers to be made from a library of monomer units. More recently, direct (hetero)arylation polymerization approaches provide a more economical route to conjugated polymers, avoiding halogenation steps in the reaction scheme.[9] Direct arylation protocols often rely on heteroatoms to increase reactivity and guide reactivity to specific positions of the monomers.[10] The conformational flexibility of the resulting polymers, due to the single-bond connectivity, provides solubility in common organic solvents, making the materials suitable for solution processing. A potential downside of this flexibility is that it adds disorder to the polymer structure. This disorder may be considered in two ways; the rotation about the single bond can oscillate by small deviations in dihedral angle due to thermal energy (dynamic disorder), or the bond can rotate by a larger amount over a higher energetic barrier and into a separate potential energy well to afford a different conformer (static disorder). To assess the effects of structural change on polymer conformation, the most common approach is to model the variation in molecular energy as a function of rotation about the single bond *via* computational methods such as density functional theory (DFT).[11,12] For each data point, the atoms involved in the torsion in question are fixed at a given angle, while the rest of the atoms are free to move in a geometry relaxation calculation. The total energies at each dihedral angle are compared, usually to the lowest energy conformation, resulting in a torsional potential energy surface (PES, Figure 1). From the PES, researchers can determine relative energies of energetic minima, barrier heights for rotation between conformers, statistical distribution of conformers,[13] as well as expected fluctuation around a minimum energy structure by assessing the steepness of the PES curve in relation to thermal energy ($kT$ is approximately 0.6 kcal/mol at room temperature). The choice of computational method influences the magnitude of energetic barriers,[14] and so care should be taken in choosing appropriate methodology. Torsional PESs based on DFT computations are used in the creation of custom force fields for molecular dynamics simulations, particularly for conjugated systems.[15]

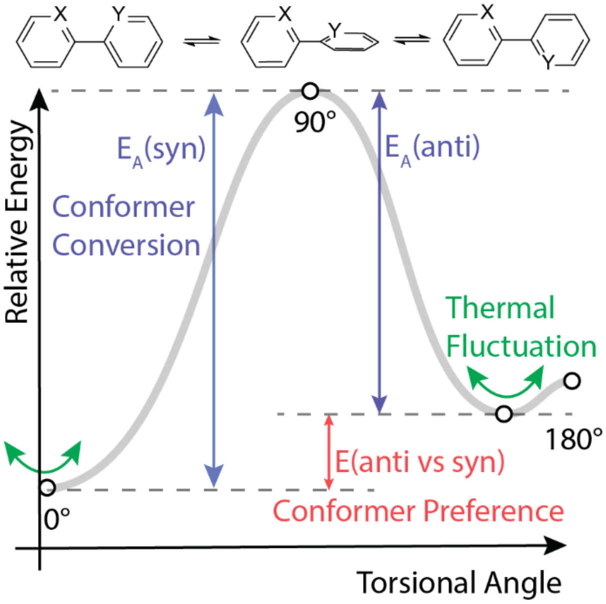


*Figure 1. Key features of a typical torsional PES (relative molecular energy versus X-C-C-Y torsional angle), highlighting rotational barrier heights akin to activation energies of reactions ($E_A$) and the difference in energetic minima which influences the preference of one conformer over another.*

## 2.2. Non-Covalent "Conformational Locks"

A main effect of heteroatoms in OSC materials has been their influence on the torsional PES, in general introduced to make the system more planar to maximize intra-chain conjugation by more efficient π-π overlap. The seminal work of Jackson et al. popularized the term "conformational lock" in organic materials design[16] although other works had discovered and investigated these effects prior,[17,18] while the "conformational lock" term is not limited to the organic electronics field.[19] This work described the gas-phase torsional PES of model systems based on two connected heterocycles common to OSC materials. The findings related the more planar structures of some systems to very short distance non-covalent interactions (NCIs) between heteroatoms of adjacent rings. The results of this study remain valid; however, the community has perhaps taken the findings out of context in more recent years. The concept has spawned a multitude of OSC structures claiming that adjacent heterocycles are locked into the as-drawn conformational structure in the presence of these close contacts, but often without supporting evidence such as full DFT torsional PES or relevant experimental data. Given recent interest in sulfur interactions, it has perhaps been lost in recent years that the authors of the 2013 paper did not themselves consider these interactions strong enough to provide any kind of "conformational lock" as illustrated by the relative strength of intermolecular model interactions in Table 1. Nevertheless, these weak non-covalent interactions have still proven useful in the design of many OSC materials.[20]

*Table 1. Computed intermolecular interaction energies between various heteroatomic groups commonly considered as conformational locks despite being weak or non-binding interactions.*[16]

| **Interaction** | **Binding energy (kcal/mol)** | **Equilibrium distance (Å)** |
|---|---|---|
| CH-N | 2.20 | ~2.5 |
| CH-O | 1.86 | ~2.4 |
| CH-F | 0.94 | ~2.5 |
| CH-S | 0.74 | ~3.1 |
| S-S | 0.72 | ~4.0 |
| O-S | 0.51 | ~3.4 |
| N-S | 0.46 | ~3.8 |
| F-S | 0.44 | ~3.4 |
| N-F | non-binding | N/A |
| O-F | non-binding | N/A |
| O-N | non-binding | N/A |

## 3. Other contributing factors to PES

### 3.1. Role of conjugation

So, if the non-covalent interactions in the OSC chains are not always attractive, or only weakly so, why do torsional PES indicate (close to) planar geometries in many cases? The main driving force for planar geometries is the increased conjugation between the two adjacent π-systems,[21,22] thankfully the same effect that is desirable for OSC materials. The 90 ° conformer is usually the highest in energy, as there is no conjugation between the two perpendicular π-systems, as well as minimal NCIs between the rings due to larger interatomic distances. Stabilization from hyperconjugation[23] by donation of neighboring lone pairs or σ-bonds into π* orbitals can be found at these orthogonal geometries, but the stabilization energy of these interactions is small in comparison to π-conjugation benefits. As the inter-ring bond is rotated to planarize the system, the system becomes more stabilized by conjugation, until a minimum energy point at 0 or 180° due to maximal π-π overlap (Figure 3, blue curve). Since DFT functionals can cause errors in delocalization lengths due to self-interaction errors,[14] it is clear now how the torsional PES can be influenced by the choice of computational method, since the stabilization by conjugation plays an important role in the PES. The inclusion of NCIs on the right-hand side of Figure 3 can have various effects when these atoms become close in space (i.e. close to planar geometries). Stabilizing NCIs (Figure 3, red) deepen the potential energy well compared to the conjugation curve. However, there are also increased steric demands particularly as the atoms become ever closer in space, which can cause an increase in potential energy and a non-planar energetic minimum (Figure 3, right-hand side). The effects of conjugation on torsional potential are very clearly observed in materials bearing formal double bonds between adjacent rings.[24] Since there is an even greater energetic penalty to rotation, interconversion of isomers is now virtually impossible, while often unfavorable NCIs between juxtaposed atoms can cause deviation from a planar geometry.[25]

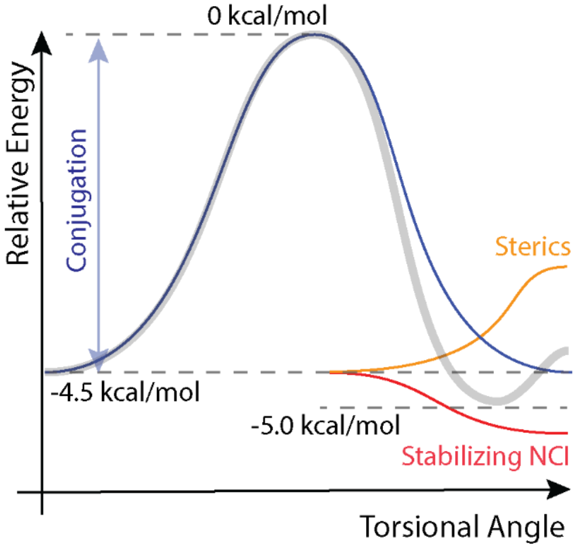


*Figure 2. Contributions of conjugation (blue curve) and NCIs (right side only, stabilizing interaction in red, destabilizing steric repulsion in orange) to a fictional torsional PES (grey curve). Estimates of energetic magnitudes are derived from reference 16 as explained in the main text.*

As a comparison of relative stabilization energies of conjugation and NCIs, the intermolecular models from Jackson (Table 1) predict binding energies of less than 1 kcal/mol at ideal separations (e.g. -0.51 kcal/mol at 3.4 Å for S-O interactions). Interatomic distances measured in their model structures are not at these ideal distances due to the covalent framework making up the molecule. Using the Morse potential fitting provided by Jackson, estimates of binding energies at these S-O distances are smaller (-0.35 kcal/mol at 3.0 Å) or even repulsive (+0.2 kcal/mol at 2.7 kcal/mol), although the different alignments in inter- versus intra-molecular models might impact these estimates. The model systems containing these S-O NCIs have rotational barriers between 3 and 5 kcal/mol, and so the contribution of these NCIs is at best 10% of the stabilization of the more planarized geometries versus the 90° conformer, the rest of the c.a. 5 kcal/mol stabilization stemming from increased conjugation (Figure 2).

## 3.2. Balancing attractive and repulsive forces

Given the different contributions of different energetic components to the torsional PES in Figure 2, computational analysis of intramolecular effects is difficult. Several studies have attempted to describe intramolecular effects, which while not perfect do support the general findings of intermolecular models. These include fragmented energy decomposition analysis,[26] analysis of electron density paths through atoms-in-molecules,[27,28] or hydrogenated models[29] to explore conjugation effects. Many of the effects work in tandem; a shorter through-space bond between heteroatoms results in greater conjugation in the shorter C-C bond, but also greater steric repulsion between all atoms involved. Addition of heteroatoms also alters the spatial distribution of the π electrons, which in turn can affect the delocalization across the rotatable bond.[21] At short distances, electrostatic interactions seem to become more important than the longer-range dispersion forces,[26] in part because the nuclei penetrate into the electron cloud of neighboring atoms, resulting in interatomic distances which are shorter than the sum of van der Waals' radii. *This short* *distance does not mean there is a net attractive force between the atoms*, since the electron-electron repulsion can be overwhelmingly large, yet the atoms occupy this space due to the covalently bonded molecular framework. In analyzing non-covalent interactions, researchers must weigh the benefits of increased conjugation, electrostatic stabilization, or resonance effects with accompanying destabilizing forces. While the main destabilizing force is the exchange repulsion / steric hindrance, electrostatic interactions may also be repulsive, and can contribute to destabilized and non-planar geometries.

Just as important, we must always consider *all* close atomic interactions. For every S-F interaction, there is an adjacent repulsive alkyl chain interaction, or more stabilizing non-traditional hydrogen bond which might play a greater role than the weak chalcogen bond (vide infra).[30] Figure 3 depicts the torsional PES of a simple thiophene-benzothiadiazole molecule, fluorinated in different positions. When the thiophene is fluorinated[31] (red structures), the preferred geometry is with a dihedral angle of 0° due to attractive S-N and H-F interactions, while the 180° conformer is disfavored due to steric clashes and electrostatic repulsion between partially negative F and N atoms. This PES suggests that the substitution pattern should aid in biasing conformation towards 0°, since any torsions in the higher energy potential well can easily overcome the shallow rotational barrier and fall to the global minimum energy structure. Fluorination of the benzothiadiazole[32] (blue structures) does not achieve the same effect, since both anti- and syn- conformers possess generally stabilizing NCIs. There is no clear preference for one conformer and the rotational barrier remains accessible to interconversion, and so there is no "conformational lock". This fluorination pattern is in fact less locked than the non-fluorinated derivative (black structures), where minima are of similar energies (despite differing optimal dihedral angles), but the non-fluorinated system has a higher rotational barrier. From the comparison of these three torsional PES and the corresponding chemical structures, the presence of heteroatom interactions alone does not dictate whether there is such a conformational lock, but rather the system as a whole needs to be considered, looking at interactions throughout the system and considering potential interactions in the opposite conformer.

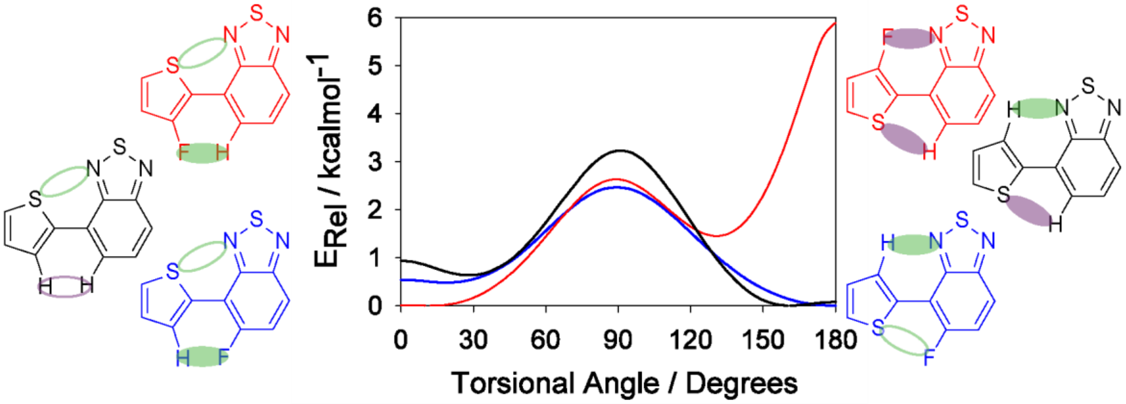


*Figure 3. Torsional PES of thiophene-benzothiadiazoles with differing fluorination pattern. Ovals indicate favorable (green) and unfavorable (purple) NCIs, filled ovals indicating a stronger interaction than the open ovals. PES computed using ωB97XD/6-31G* in gas phase.*

## 3.3. Remote atom effects on torsional PES

In some cases, even heteroatoms that are not directly involved in NCI in proximity to the bond being rotated can affect its torsional PES. Skabara and colleagues reported on a range of fluorinated phenylene/thiophene systems.[33] Perhaps surprisingly, remote fluorination can enhance non-traditional hydrogen bonds affecting torsional PES on the opposite side of the molecule. The electron withdrawing effect of the fluorine atoms results in the proton having even less share of the electron density and therefore a greater partial positive charge, leading to stronger NCI with the partial negative charges of oxygen atoms on the adjacent thiophene ring. This effect is also apparent in the structures in Figure 4, where the 0° conformers of the two fluorinated isomers possess the same NCIs as-drawn, but variations in electronic structure affect the partial charges and electron distribution in the system,[21] thus changing the strength of the NCI.

## 4. Consequences of Torsional PES Features

### 4.1. Conformer conversion

The conversion between different conformers has been investigated by Risko and colleagues[21] for a series of photovoltaic small molecule OSCs from the Bazan lab.[34] Molecular dynamics simulations (Figure 4), based on custom force fields derived from torsional PES, show the rapid rotation and almost random distribution of simple thiophene-thiophene bonds ("blue"), whereas benzothiadiazole rotation is drastically stalled due to stronger non-traditional hydrogen bonding ("green"). Inclusion of fluorine atoms on the benzothiadiazole makes seemingly small differences to the dynamics of this torsion ("red"), while the paper goes on to explore the role of solvent additives to the conformational bias. The conversion between different conformers is more directly related to the barrier height of the torsional PES, rather than an energetic minimum being planar or being more stable than another minimum.

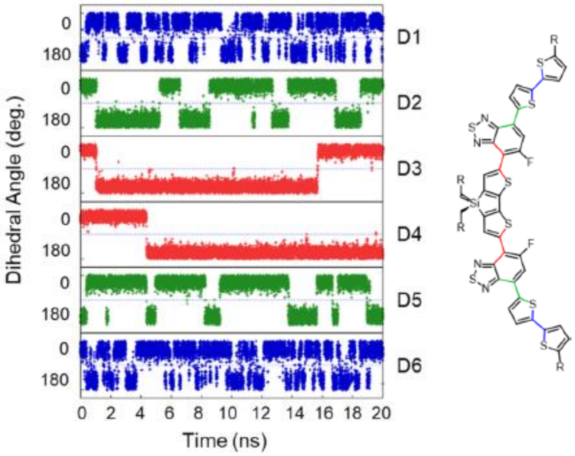


*Figure 4. Molecular dynamics study on interconversion of different conformations in a photovoltaic small molecule. Adapted from Reference 13 with permission. Copyright 2021 American Chemical Society.* [21]

### 4.2. Is more planar even important?

In the context of conjugated framework planarity, an interesting conclusion was drawn by computational analysis by Wheeler et al., where the importance of a planar geometry of isolated chains was questioned.[35] The torsional PESs of a series of oligothiophenes were calculated in the presence of other neighboring oligothiophene chains, as opposed to the usual gas- or solution-phase *in silico* environments. While oligothiophenes in the gas phase exhibit energetic minimum characterized by a 150 ° inter-ring dihedral angle, the "solid-state" torsional PES show a planar geometry with a 180 ° dihedral angle. Perhaps more importantly, the torsional PES is incredibly steep in this environment, rendering the interconversion of conformers impossible. These theoretical results match experimental data, since bithiophene is known to have a planar geometry in its crystal structure,[36] due to additional solid-state intermolecular forces. These results suggest that the dihedral angles of gas- or solution-phase energetic minima are perhaps not that important, and rather other features of the torsional PES are more influential; i.e. the barriers for rotation between energetic minima which influence the rate of conversion and the distribution of syn/anti conformers, which become locked in place in the solid-state environment. It should be noted that in the case of polymers and small molecules with many degrees of freedom, the solid-state environment in thin-film devices is typically amorphous or semi-crystalline, and thus the preferred conformations and torsional rigidity might also deviate from single crystal models due to variation in intermolecular interactions.

## 4.3. Experimental evidence

While much of the discussion thus far is based on computed torsional PES and electronic structure, there are a few experimental techniques that can be used to determine the influence of non-covalent interactions. $^1$H and $^{19}$F NMR spectroscopy has been used to show the different environments of these atoms within a small molecule non-fullerene acceptor.[37] Crystals grown from different solvents showed different amounts of disorder for the relative sulfur and fluorine positions. Dissolving the crystals for solution NMR experiments, initial spectra mirrored the conformational occupations found in the crystals, but over time the system equilibrated to yield multiple peaks as the functional groups were allowed to rotate and occupy their preferred orientations.

An interesting report on interconversion of quinoidal thiophene oligomers highlights the presence of non-covalent S-F bonds favoring one isomer over another.[38] Due to the quinoidal structure, the thiophene rings are unable to rotate relative to one another due to a formal double bond between them and are thus distinguishable by spectroscopic means. The closed-shell quinoidal structure exists in an equilibrium with an open-shell diradical form, the radicals located at opposite ends of a regular thiophene oligomer, which can undergo bond rotations due to thermal energy. In the case of the non-fluorinated oligomer, the $^1$H NMR spectrum shows a mixture of cis/trans isomers, while $^{19}$F NMR of the fluorinated oligomers show only one all-trans isomer. The authors highlight the role of S-F interactions in biasing the conformation of the diradical forms, which get locked into a single isomer upon quinoidalization. DFT optimized structures were used to compare isomers along with natural bond order analysis to look at the NCIs, but a full torsional PES, particularly of the diradical form, would provide even more information on the interconversion of conformers than just the optimized structures.

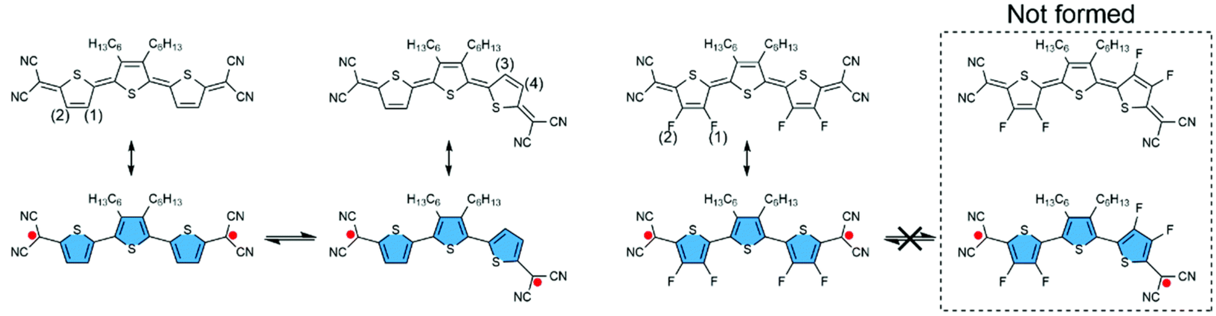


*Figure 5. Interconversion of quinoidal thiophene oligomers via diradical intermediates was observed by NMR spectroscopy for non-fluorinated species (left) but not for fluorinated ones (right), due to the influence of S-F NCIs. Adapted from reference 29 with permission. Copyright 2020 Royal Society of Chemistry* [38]

Numerous crystal structures show close heteroatomic contacts which align well with computed PES, albeit also influenced by solid-state packing effects.[8] The use of X-ray diffraction to prove relative abundance of conformers can be problematic in that the crystals may not reflect the distribution in solution, as one conformer may preferentially crystallize over another. Aggregate states of different conformers have shown different optical properties, depending on the heteroatom interactions in the oligomer / polymer systems.[39,40] Ultimately, device properties can be related to chemical structure, although this is an ensemble of effects including not only non-covalent intramolecular interactions but also solid-state packing, interchain charge transport, aggregate effects and so on.

## 5. Polymer Systems

### 5.1. Charge distribution in polymers

In addition to the effects on structure, planarity, and conformational order, inclusion of heteroatoms into a polymer backbone can affect the electronic properties. Exchanging carbon or hydrogen for heteroatoms naturally results in polarization of the covalent bonds due to differences in electronegativity of the atoms involved. The ability for heteroatoms to better stabilize positive or negative charges through both inductive and resonance effects might lead to charge localization at points of the polymer chain. Heteroatoms also change the aromaticity of the conjugated system. Thus, while polyphenylene already possesses a stable electronic arrangement of adjacent aromatic Clar sextets, heterocycles such as thiophene are less aromatic than benzene and will more readily change their electronic structure to accommodate additional charges. This can be visualized from DFT calculations,[41] where the distribution of the excess charge upon a redox event or optical absorption can be used to gain information on chemical structure – electronic property relationships. This approach has been used in explaining differences in stability between co-polymers where benzodithiophene was paired with different monomers, where the residual charge on the benzodithiophene made it susceptible to chemical oxidation leading to polymer degradation. Examining the charge-per-monomer in donor-acceptor polymers can reveal information of the roles of each heterocyclic group in the overall electronic structure of the polymer, used for example in balancing electron-rich and -poor regions for ambipolar charge transport. The other, perhaps more obvious, effect of changes to the electronic distribution by inclusion of heteroatoms is the change in redox properties (i.e. ionization potential and electron affinity) and optical absorption.

### 5.2. Regioisomers based on side chain placement

An interesting comparison occurs when the same side chains (capable of forming stabilizing NCIs with heteroatoms in the conjugated system) are used at different points along the polymer chain in regio-isomeric polymers.[42,43] This has become increasingly relevant in recent years with the emergence of bioelectronic applications and a renewed interest in semiconductor:dopant interactions for thermoelectric applications. These new directions have spurred the community to incorporate highly polar side chains, for instance oligoether based chains, and design highly electron-rich p-type systems, often taking advantage of mesomeric effects from side chain heteroatoms. These side chains affect different bond torsions along the polymer backbone through interactions of alkoxy oxygen atoms and the sulfur atoms of the thiophene rings. This can occur in an additive manner where multiple groups serve to influence the same inter-ring bond with greater effect but leave another bond without any additional NCI influence (Figure 6, “in” isomer). By relocating side chains in the polymer repeat unit, it is possible instead to influence multiple bond torsions in the polymer chain, but each to a lesser degree than the first (additive) case as illustrated for a dithienophenylene system in Figure 6 (“out” isomer). Despite the S-O interactions between flanking thiophenes and the glycolated phenylene having similar stabilization strengths in each polymer, the “in” isomer possesses a more consistent backbone structure due to similar dihedral angles along the chain, as well as a greater tendency to adopt the as-drawn structure because of an energetic penalty in rotating the thiophene-phenylene bond to the opposing conformer. These “conformational locking” effects originate less from any stabilizing S-O NCIs and more from the steric and electrostatic repulsion of the close proximity of two glycol chains in the alternate conformation.

In addition to the influence on polymer conformation, these regioisomers will also have different charge distribution within the polymer chain, since the typical peripheral heteroatoms (e.g. halides or oxygen-containing functionalities) are able to donate lone pairs by resonance or have an electron withdrawing effect by induction. Placing the side chains close together results in regions of the polymer backbone which are more electron-rich, in the case of net electron-donating chains. This may influence the size of polarons formed in the polymer, which has direct influence on charge transport within the polymer backbone as well as inter-chain transport with neighboring polymer strands. The bar charts in Figure 6 show that when a polymer constructed of the "out" isomer of the repeating unit undergoes one-electron oxidation, the charge is greatest on an unsubstituted thiophene group, and spreads onto adjacent glycolated groups. This minimizes the disruption of loss of aromaticity of the benzenoid rings. In contrast, when the oligoether chains are more clustered together in the "in" isomer, the excess positive charge is more stabilized on the phenylene ring surrounded by electron donating oligoether chains. The "in" isomer exhibited a four-fold higher charge mobility and a six-fold better organic electrochemical transistor performance than the "out" isomer, attributed to a combination of polymer backbone torsional profile and charge distribution, and longer-range crystalline order despite the "out" isomer exhibiting closer π-π stacking.

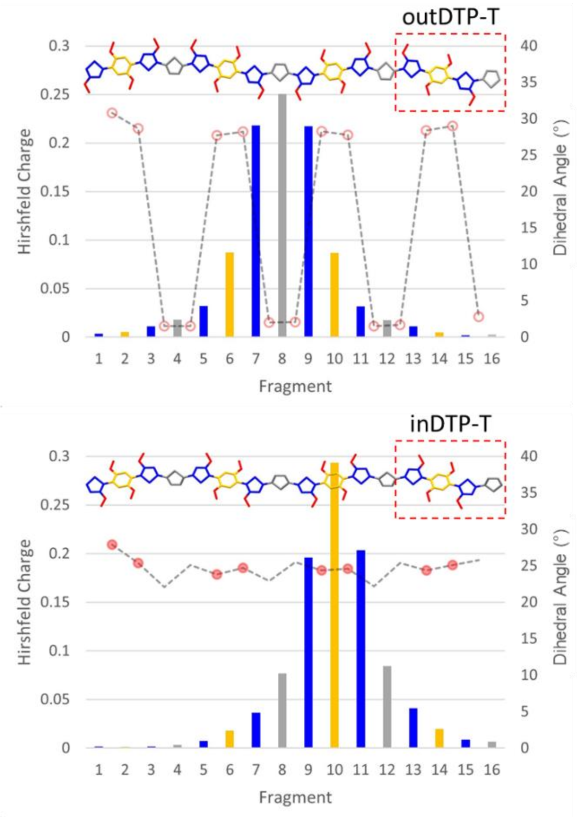


*Figure 6. Charge distributions (bar charts) and dihedral angles (scatter plots) along phenylene-thiophene polymers differing only by the placement of oligoether side chains. Adapted from reference 34.*

It is quite straightforward to separate the contributions of the geometric variation by NCIs and the distortion of electronic delocalization through DFT calculations.[42] Structures can be optimized with side chains in place to gain torsional effects from NCIs. After removal of the side chains without geometry re-optimization, calculations to gain the electronic structure in the absence of resonance and inductive effects can be used to gauge the contributions from structural and electronic effects. In the case of the glycolated polythiophenes, the planarization by NCIs was determined to be a minor factor to electron delocalization by DFT calculations, instead the electronic effects of the oligoether groups dominated the per-thiophene charge distributions.[42] The more uniform placement of oligoether chains along the polymer resulted in better organic electrochemical transistor performance than the clustering of these chains close to one another, this being attributed to the more consistently planar polymer backbone, the more even charge distribution across multiple repeat units, the thin film morphology, as well as increased water uptake into the film influenced by side chain spacing.

### 5.3. Interactions between Side chains

P3HT is 65 % alkyl chain by atom count and nearly 50 % by mass, so the solubilizing chains should have a large influence on polymer properties, including torsional profile along the polymer chain. A comparison between alkyl and oligoether solubilizing chains was performed by Moro et al.,[44] where interactions between chains influenced the conformation of the conjugated polymer backbone. Polymers were deposited as monolayers and imaged by scanning tunneling microscopy, overlaying molecular models of the polymers to identify side chain alignments. While the alkyl chains interdigitate as straight (extended) chains, the oligoether chains do so via more complex chain twisting due to a mixture of electrostatic and dispersion forces between chains. Molecular dynamics studies suggest that the interactive forces between the side chains were stronger than the torsional potentials between thiophene groups alone, and thus the side chain interdigitation modes could bias the conformation of the polymer in the solid-state. In fact, the more uniform side chain interactions between alkyl chains resulted in fewer kinks in the polymer backbone structure than the oligoether polymers, despite the presence of S-O interactions along the polymer chain in the latter.

## 6. Conclusions

As a prime motive for the last decade, the influence of heteroatoms on torsional potentials and hence electronic properties of organic semiconductors might have been overstated. These short distance non-covalent interactions are weak in comparison to the gain in stabilization by increased conjugation in planarized π-systems and can be overridden by intermolecular packing effects in the solid-state. On the other hand, benefits of heteroatom incorporation include changes in spatial charge distribution and local aromaticity which likely have just as great an influence on polymer properties as torsional variance. So, as to what is the role of heteroatoms in conjugated polymers? In terms of the torsional potentials, their greatest influence is in biasing one conformer over another, resulting in more ordered polymer chains which become “locked” or planarized not by the weak non-covalent interactions but the trapping in environments where rotation is limited. This is likely to lead to stronger registry between polymer chains and therefore more favorable solid-state packing. Electronically, heteroatoms can influence polymer properties by adjusting redox potentials and by affecting charge (de)localization along the polymer backbone. Their role in allowing reactivity through e.g. direct arylation cross-coupling and regioselectivity during synthesis should also not be overlooked. Suffice to say, including heteroatoms for the sole purpose of “conformational locking” should be considered with more thought and a greater communication between theoretical and synthetic chemists is required.

## Acknowledgements

C.B.N. acknowledges the European Commission for financial support through the MITICS H2020-EU-FET Open project (No. 964677).

## Conflict of Interests

The authors declare no conflict of interest.

## References

[1] H. Bronstein, C. B. Nielsen, B. C. Schroeder, I. McCulloch, *Nat Rev Chem* **2020**, *4*, 66–77.

[2] X. Guo, A. Facchetti, *Nat Mater* **2020**, *19*, 922–928.

[3] R. D. McCullough, R. D. Lowe, M. Jayaraman, D. L. Anderson, *Journal of Organic Chemistry* **1993**, *58*, 904–912.

[4] H. Bronstein, M. Hurhangee, E. C. Fregoso, D. Beatrup, Y. W. Soon, Z. Huang, A. Hadipour, P. S. Tuladhar, S. Rossbauer, E. H. Sohn, S. Shoaee, S. D. Dimitrov, J. M. Frost, R. S. Ashraf, T. Kirchartz, S. E. Watkins, K. Song, T. Anthopoulos, J. Nelson, B. P. Rand, J. R. Durrant, I. McCulloch, *Chemistry of Materials* **2013**, *25*, 4239–4249.

[5] S. C. Price, A. C. Stuart, L. Yang, H. Zhou, W. You, *J Am Chem Soc* **2011**, *133*, 4625–4631.

[6] Z. Fei, P. Boufflet, S. Wood, J. Wade, J. Moriarty, E. Gann, E. L. Ratcliff, C. R. Mcneill, H. Sirringhaus, J. S. Kim, M. Heeney, *J Am Chem Soc* **2015**, *137*, 6866–6879.

[7] C. Sutton, C. Risko, J. L. Brédas, *Chemistry of Materials* **2016**, *28*, 3–16.

[8] J. Cameron, A. L. Kanibolotsky, P. J. Skabara, *Advanced Materials* **2023**, 2302259.

[9] J. F. Ponder, B. Schmatz, J. L. Hernandez, J. R. Reynolds, *J Mater Chem C Mater* **2018**, *6*, 1064–1070.

[10] T. Bura, J. T. Blaskovits, M. Leclerc, *J Am Chem Soc* **2016**, *138*, 10056–10071.

[11] S. Sharma, M. Bendikov, *Chemistry – A European Journal* **2013**, *19*, 13127–13139.

[12] Y. H. Wijsboom, Y. Sheynin, A. Patra, N. Zamoshchik, R. Vardimon, G. Leitus, M. Bendikov, *J Mater Chem* **2011**, *21*, 1368–1372.

[13] Y. Che, D. F. Perepichka, *Angewandte Chemie International Edition* **2021**, *60*, 1364–1373.

[14] V. Bhat, C. P. Callaway, C. Risko, *Chem Rev* **2023**, *123*, 7498–7547.

[15] M. Casalegno, A. Famulari, S. V. Meille, *Macromolecules* **2022**, *55*, 2398–2412.

[16] N. E. Jackson, B. M. Savoie, K. L. Kohlstedt, M. Olvera De La Cruz, G. C. Schatz, L. X. Chen, M. A. Ratner, *J Am Chem Soc* **2013**, *135*, 10475–10483.

[17] M. Turbiez, P. Frère, P. Blanchard, J. Roncali, *Tetrahedron Lett* **2000**, *41*, 5521–5525.

[18] B. M. Medina, D. Wasserberg, S. C. J. Meskers, E. Mena-Osteritz, P. Bäuerle, J. Gierschner, *Journal of Physical Chemistry A* **2008**, *112*, 13282–13286.

[19] D. Dey, S. Bhandary, A. Sirohiwal, V. R. Hathwar, D. Chopra, *Chemical Communications* **2016**, *52*, 7225–7228.

[20] H. Huang, L. Yang, A. Facchetti, T. J. Marks, *Chem Rev* **2017**, *117*, 10291–10318.

[21] C. Karunasena, S. Li, M. C. Heifner, S. M. Ryno, C. Risko, *Chemistry of Materials* **2021**, *33*, 9139–9151.

[22] R. Duke, V. Bhat, A. Smith, S. Goodlett, S. Tretiak, C. Risko, *Macromolecules* **2023**, *56*, 5259–5267.

[23] W. Wei, C. Champion, Z. Liu, S. J. Barigye, P. Labute, N. Moitessier, *J Chem Inf Model* **2019**, *59*, 4764–4777.

[24] H. Hwang, D. Khim, J. Yun, E. Jung, S. Jang, Y. H. Jang, Y. Noh, D. Kim, *Adv Funct Mater* **2015**, *25*, 1146–1156.

[25] H. Chen, M. Moser, S. Wang, C. Jellett, K. Thorley, G. T. Harrison, X. Jiao, M. Xiao, B. Purushothaman, M. Alsufyani, H. Bristow, S. De Wolf, N. Gasparini, A. Wadsworth, C. R. McNeill, H. Sirringhaus, S. Fabiano, I. McCulloch, *J Am Chem Soc* **2021**, *143*, 260–268.

[26] K. J. Thorley, I. McCulloch, *J Mater Chem C Mater* **2018**, *6*, 12413–12421.

[27] J. R. Lane, J. Contreras-García, J.-P. Piquemal, B. J. Miller, H. G. Kjaergaard, *J Chem Theory Comput* **2013**, *9*, 3263–3266.

[28] S. Shahbazian, *Chemistry - A European Journal* **2018**, DOI 10.1002/chem.201705163.

[29] A. T. Kleinschmidt, A. X. Chen, R. S. Ramji, T. A. Pascal, D. J. Lipomi, *J Phys Chem B* **2023**, *127*, 2092–2102.

[30] G. Conboy, H. J. Spencer, E. Angioni, A. L. Kanibolotsky, N. J. Findlay, S. J. Coles, C. Wilson, M. B. Pitak, C. Risko, V. Coropceanu, J. L. Brédas, P. J. Skabara, *Mater Horiz* **2016**, *3*, 333–339.

[31] C. Roy, T. Bura, S. Beaupré, M. A. Légaré, J. P. Sun, I. G. Hill, M. Leclerc, *Macromolecules* **2017**, *50*, 4658–4667.

[32] Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade, H. Yan, *Nat Commun* **2014**, *5*, 1–8.

[33] T. Kharandiuk, E. J. Hussien, J. Cameron, R. Petrina, N. J. Findlay, R. Naumov, W. T. Klooster, S. J. Coles, Q. Ai, S. Goodlett, C. Risko, P. J. Skabara, *Chemistry of Materials* **2019**, *31*, 7070–7079.

[34] C. McDowell, K. Narayanaswamy, B. Yadagiri, T. Gayathri, M. Seifrid, R. Datt, S. M. Ryno, M. C. Heifner, V. Gupta, C. Risko, S. P. Singh, G. C. Bazan, *J Mater Chem A Mater* **2018**, *6*, 383–394.

[35] E. C. Vujanovich, J. W. G. Bloom, S. E. Wheeler, in *Journal of Physical Chemistry A*, American Chemical Society, **2012**, pp. 2997–3003.

[36] M. Pelletier, F. Brisse, *Acta Crystallogr C* **1994**, *50*, 1942–1945.

[37] Y. Zhang, C. Yu, T. Shan, Y. Chen, Y. Wang, M. Xie, T. Li, Z. Yang, H. Zhong, *Cell Rep Phys Sci* **2022**, *3*, 100765.

[38] K. Yamamoto, S. I. Kato, H. Zajaczkowska, T. Marszalek, P. W. M. Blom, Y. Ie, *J Mater Chem C Mater* **2020**, *8*, 3580–3588.

[39] S. Wedler, A. Bourdick, S. Athanasopoulos, S. Gekle, F. Panzer, C. McDowell, T. Q. Nguyen, G. C. Bazan, A. Köhler, *J Mater Chem C Mater* **2020**, *8*, 4944–4955.

[40] S. Wedler, C. Zhou, G. C. Bazan, F. Panzer, A. Köhler, *Journal of Physical Chemistry Letters* **2020**, *11*, 9379–9386.

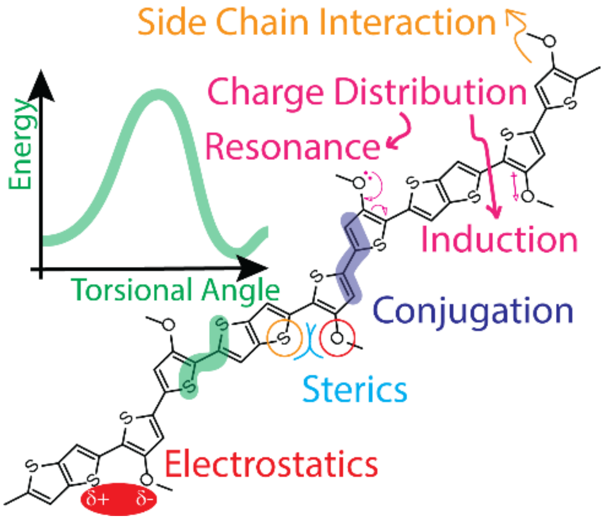
[41] K. J. Thorley, *Journal of Physical Chemistry B* **2023**, *127*, 5102–5114.

[42] R. K. Hallani, B. D. Paulsen, A. J. Petty, R. Sheelamanthula, M. Moser, K. J. Thorley, W. Sohn, R. B. Rashid, A. Savva, S. Moro, J. P. Parker, O. Drury, M. Alsufyani, M. Neophytou, J. Kosco, S. Inal, G. Costantini, J. Rivnay, I. McCulloch, *J Am Chem Soc* **2021**, *143*, 11007–11018.

[43] R. Halaksa, J. H. Kim, K. J. Thorley, P. A. Gilhooly-Finn, H. Ahn, A. Savva, M. Yoon, C. B. Nielsen, *Angewandte Chemie International Edition* **2023**, *62*, e202304390.

[44] S. Moro, N. Siemons, O. Drury, D. A. Warr, T. A. Moriarty, L. M. A. Perdigão, D. Pearce, M. Moser, R. K. Hallani, J. Parker, I. McCulloch, J. M. Frost, J. Nelson, G. Costantini, *ACS Nano* **2022**, *16*, 21303–21314.

## Table of Contents



Organic semiconductors often contain heteroatoms to influence torsional potentials by so-called "conformational locks". These non-covalent interactions, however, contribute less to planarization than generally assumed. Greater influences arise from stabilization by conjugation, consideration of steric repulsion, and interactions involving solubilizing chains or neighboring moieties in solid state.

## Biographies

Karl Thorley obtained his D.Phil in 2010 under the supervision of Prof. Harry Anderson at the University of Oxford. Following postdoctoral research stays at Universität Würzburg, University of Kentucky and Imperial College London, he returned to the University of Kentucky where he currently holds a Research Scientist position at the Center for Applied Energy Research. His research has dealt with a wide range of organic electronic and optical materials, with expertise in synthesis, characterization and computational analysis of small molecule semiconductors and conjugated organic polymers.

Christian Nielsen received his PhD from the University of Copenhagen in Denmark in 2004. He joined Queen Mary University of London in 2016 and is currently Reader in Organic Materials in the Department of Chemistry within the School of Physical and Chemical Sciences. His research focuses on the design and synthesis of new semiconducting materials for organic electronic and bioelectronic applications with the aim of elucidating important structure-property relations and providing new tailored materials to advance the understanding and performance of organic electronic and bioelectronic devices.