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***The Wide Extent of Reactivity Descriptors Applicability: From Chemical
Pathway Predictor to Charge Transference and Transport Description***

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Pathway Predictor to Charge Transference and Transport Descriptor***

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Aos 29 dias do mês de abril do ano de 2025, às 8h, no(a) por videoconferência, realizou-se a defesa de TESE DE DOUTORADO de GABRIEL GOMES BALTAZAR ALVES, intitulada **The Wide Extent of Reactivity Descriptors Applicability: From Chemical Pathway Predictor to Charge Transference and Transport Description**. A Comissão Examinadora foi constituída pelos seguintes membros: Prof. Dr. AUGUSTO BATAGIN NETO (Orientador(a) - Participação Virtual) do(a) Departamento de Ciências e Tecnologia / Instituto de Ciências e Engenharia - Unesp/Câmpus de Itapeva da , Profa. Dra. CHRISTINE LARTIGAU-DAGRON (Participação Virtual) do(a) Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux (Institut - IPREM) / Université de Pau et des Pays de l'Adour - UPPA/França, Profa. Dra. PAULA HOMEM DE MELLO (Participação Virtual) do(a) Centro de Ciência Naturais e Humanas / UNIVERSIDADE FEDERAL DO ABC, Profa. Dra. CLARISSA DE ALMEIDA OLIVATI (Participação Virtual) do(a) Departamento de Física / Faculdade de Ciência e Tecnologia - Unesp/Câmpus de Presidente Prudente, Prof. Dr. RAFAEL PLANA SIMÕES (Participação Virtual) do(a) Departamento de Bioprocessos e Biotecnologia / Faculdade de Ciências Agrônômicas de Botucatu - Unesp. Após a exposição pelo doutorando e arguição pelos membros da Comissão Examinadora que participaram do ato, de forma presencial e/ou virtual, o discente recebeu o conceito final: **APROVADO** . Nada mais havendo, foi lavrada a presente ata, que após lida e aprovada, foi assinada pelo(a) Presidente(a) da Comissão Examinadora.

Prof. Dr. AUGUSTO BATAGIN NETO

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Dedication

To my wife Lana, my parents Getúlio and Glória, my siblings Victor, Gabriela, Ana Clara, and all my family.

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Firstly, I'd like to thank my parents, Getulio and Glória, for giving me the miracle of life and allowing me to experience life and all it has to offer. Also, thank them for the education they'd given me and the moral values they taught, which I always carry with me.

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*“Learn from yesterday, live for today, and hope for tomorrow. The important thing is not to
stop questioning.”*

Albert Einstein (1879 - 1955)

Resumo

O uso de ferramentas teórico-computacionais na ciência de materiais data da década de 70. Naturalmente, com o aumento do poder computacional, aumentou-se também a complexidade, precisão e confiabilidade dos métodos computacionais. Hoje, algumas escolhas metodológicas, como a escolha de um funcional de correlação e troca, podem aumentar o custo computacional em pelo menos uma ordem de grandeza, significando um custo energético considerável. É possível, porém, utilizar-se de ferramentas computacionalmente mais econômicas, mas ainda assim, confiáveis pelo seu embasamento teórico. Este trabalho utiliza-se desses métodos para explorar soluções em dois temas distintos: *i*) Compreender, em escala molecular, as características e propriedades responsáveis por tornar o par doador:aceitador D18:Y6, o paradigma de eficiência em conversão de energia solar; *ii*) Investigar caminhos químicos não explorados da evolução do composto 1-azafulvenaleno em fenilnitreno. Dentre as diversas opções metodológicas destacam-se os descritores de reatividade, em específico, os índices de Fukui condensado aos átomos e a maciez química local, que são de baixo custo computacional, e trazem resultados confiáveis quanto a descrição de interação com agentes externos, e interação intramolecular, respectivamente. Ambos dependem apenas de cálculos de energia/ponto único de energia, os quais são feitos considerando a teoria do funcional da densidade. Essas abordagens, em consonância com alguns outros descritores, permitiram descrever rotas de transferência de carga, evidenciar em escala molecular as capacidades de doação/aceitação de elétrons, diferenciando os bons e maus pares doador:aceitador para aplicação em camada ativa de célula solar. Além disso, rotas químicas completas para o 1-azafulvenaleno foram encontradas, mostrando as interações utilizadas, rotas alternativas e caminhos reversíveis. Os descritores escolhidos mostraram-se capazes de aplicações além de suas concepções iniciais, em especial a descrição de transferência de carga e capacidades de doador/aceitador para os índices de Fukui, e a capacidade de encontrar rotas químicas para a maciez local. Além disso, a combinação de descritores de baixo custo levaram a resultados que propõe explicações a nível molecular para comportamentos macromolecular observados experimentalmente, além de apresentar novos resultados, como os sítios de entrada de elétrons e os caminhos que estes fazem no material, e os novos caminhos químicos para a molécula alvo.

Palavras-Chave: cálculos de estrutura eletrônica; descritores de reatividade; transferência de carga; rotas químicas; célula solar orgânica.

Abstract

The use of theoretical-computational tools in materials science dates back to the 70s. Naturally, as computing power increased, so did the complexity, precision, and reliability of computational methods. Today, some methodological choices, such as the choice of a correlation and exchange functional, can increase the computational cost by at least an order of magnitude, meaning a considerable energy cost. This work employs these methods to explore solutions in two distinct areas: *i*) Understanding, at the molecular level, the characteristics and properties that make the donor:acceptor pair D18:Y6 a paradigm of efficiency in solar energy conversion; *ii*) Investigating unexplored chemical pathways in the transformation of 1-azafulvenallene into phenylnitrene. Among the various methodological options, reactivity descriptors stand out, specifically the condensed-to-atoms Fukui indices and local softness, which have low computational cost and provide reliable results for describing interactions with external agents and intramolecular interactions, respectively. Both rely solely on single-point energy calculations, which are performed using density functional theory. These approaches, in conjunction with other descriptors, have made it possible to describe charge transfer pathways, highlight electron donation and acceptance capabilities at the molecular scale, and distinguish good and poor donor:acceptor pairs for application in the active layer of solar cells. Additionally, complete chemical pathways for 1-azafulvenallene were identified, revealing the interactions involved, alternative routes, and reversible pathways. The chosen descriptors proved to be useful beyond their initial conceptions, particularly in describing charge transfer and donor/acceptor capabilities for the Fukui indices, as well as in identifying chemical pathways for local softness. Furthermore, the combination of low-cost descriptors led to results that propose molecular-level explanations for macromolecular behaviors observed experimentally. Additionally, it introduced new findings, such as the electron entry sites and their pathways within the material, as well as new chemical routes for the target molecule.

keywords: electronic-structure calculations; reactivity descriptors; charge transference; chemical pathways, organic solar cells.

Résumé

L'utilisation d'outils théoriques et computationnels en science des matériaux remonte aux années 1970. Naturellement, avec l'augmentation de la puissance de calcul, la complexité, la précision et la fiabilité des méthodes informatiques ont également progressé. Aujourd'hui, certaines décisions méthodologiques, comme le choix d'une fonctionnelle d'échange et de corrélation, peuvent accroître le coût computationnel d'au moins un ordre de grandeur, impliquant ainsi une dépense énergétique considérable. Ce travail appliqué ces méthodes pour explorer des solutions dans deux domaines distincts : i) Comprendre, au niveau moléculaire, les caractéristiques et propriétés qui font du couple donneur:accepteur D18:Y6 un paradigme d'efficacité dans la conversion de l'énergie solaire ; ii) Explorer des voies chimiques encore inexplorées dans la transformation du 1-azafulvénallène en phénylnitrène. Parmi les diverses options méthodologiques, les descripteurs de réactivité se distinguent, en particulier les indices de Fukui condensés aux atomes et la douceur locale, qui sont peu coûteux en termes de calcul et fournissent des résultats fiables pour décrire respectivement les interactions avec des agents externes et les interactions intramoléculaires. Ces descripteurs reposent uniquement sur des calculs d'énergie à point unique, réalisés dans le cadre de la théorie de la fonctionnelle de la densité. Ces approches, associées à d'autres descripteurs, ont permis de décrire des voies de transfert de charge, de mettre en évidence les capacités de donation et d'acceptation d'électrons à l'échelle moléculaire et de différencier les bons et mauvais couples donneur:accepteur pour leur application dans la couche active des cellules solaires. Par ailleurs, des voies chimiques complètes pour le 1-azafulvénallène ont été identifiées, mettant en lumière les interactions en jeu, les chemins alternatifs et les processus réversibles. Les descripteurs choisis se sont révélés utiles au-delà de leur conception initiale, notamment pour la description du transfert de charge et des capacités de donneur/accepteur à travers les indices de Fukui, ainsi que pour l'identification de voies chimiques via la douceur locale. De plus, la combinaison de descripteurs à faible coût a conduit à des résultats proposant des explications à l'échelle moléculaire des comportements macromoléculaires observés expérimentalement. Elle a également permis d'apporter de nouvelles perspectives, notamment sur les sites d'entrée des électrons et leurs trajectoires au sein du matériau, ainsi que sur de nouvelles voies de réaction pour la molécule cible.

Mots-clés : calculs de structure électronique ; descripteurs de réactivité ; transfert de charge ; voies chimiques ; cellules solaires organiques.

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Abbreviation list

A: acceptor

BHJSC: bulk heterojunction solar cell

BZTP: dithieno[3,2-b]pyrrolobenzotriazole

CAFI: condensed-to-atoms Fukui indexes

CS: closed-shell

CT: charge transfer

CTFI: charge transfer Fukui indexes

CTR: charge transfer reaction

D: donor

DOS: density of states

EES: electronic excited-state

FF: fill factor

FMO: frontier molecular orbital

GGA: generalized-gradient approximation

GTO: Gaussian-type orbitals

HF: Hartree-Fock

HK: Hohenberg-Kohn

IEO: International Energy Outlook

IRC: intrinsic reaction coordinate

IRI: interaction region indicator

KS: Kohn-Sham

LDA: local density approximation

LS: local softness

LSDA: local spin density approximation

MD: molecular dynamics

NFA: non-fullerene acceptors

NREL: National Renewable Energy Laboratory

OECD: Organisation for Economic Co-operation and Development

OS: open-shell

OSC: organic solar cell

PCE: power conversion efficiency

RR: radical reaction

SE: Schrödinger's equation

EG: end group

SMA: small molecule acceptor

STO: Slater-type orbital

TD: time-dependent

TD-DFT: time-dependent density functional theory

TF: Thomas-Fermi

TFD: Thomas-Fermi-Dirac

TDFW: Thomas-Fermi-Dirac-Weizsacker

VdW: Van der Waals

XC: exchange-correlation

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MOTIVATION

The field of material sciences is vast and multidisciplinary, leading to the adoption of various approaches for the study of similar or identical materials. The primary categorization of these approaches involves either theoretical or experimental methods. Within each of these categories, there is a vast realm to be explored. For instance, experimental studies may encompass material synthesis, characterization, and application in devices. Furthermore, the depth of exploration may extend to a myriad of synthesis and characterization methods, each of them presenting its unique set of advantages, disadvantages, and reasons for utilization.

Similarly, theoretical studies exhibit a diverse range, including developing theoretical approaches like creating new computational programs or methods for calculating material properties. Alternatively, some studies may involve applying specific tools and software to investigate material properties and behavior. Within the scope of property investigation, researchers can opt for classical physics or quantum mechanics theories, employ periodic systems, or focus on individual molecules. The vast array of options makes choosing the most suitable approach challenging, further complicated by the varying computational costs of different tools.

Opting for computationally economical tools offers several advantages. A more cost-effective method translates to faster completion, reducing energy consumption, which is beneficial to the environment. Additionally, from a scientific standpoint, quicker calculations allow more time for in-depth analysis rather than waiting for computations to conclude. However, trade-offs exist, as cheaper methods often rely on simplifications that may affect result quality. The key lies in identifying a reliable yet simple method that avoids oversimplification while producing results comparable to more intricate approaches.

Within our research group, a reactivity descriptor known as the Condensed-to-Atoms Fukui index has proven to be a cost-effective tool successfully applied across diverse systems (ALVES et al., 2020; BARBOZA; GOMES; BATAGIN-NETO, 2021; G. B. ALVES; BATAGIN-NETO, 2023; GALINDO et al., 2020; MAIA; VENTORIM; BATAGIN-NETO, 2019). These indices allow us to estimate the reactivity of atoms in a molecule, based on finite differences of the atomic electron populations, considering cationic, neutral, and anionic states. Notably, this tool serves not only as a reactivity descriptor but also reveals potential beyond its primary purpose, thanks to its unique calculation method. In the course of this investigation, this work explores the interpretation and diverse applications that these indices can offer, showcasing the versatility and broader utility of this valuable tool.

The first chapter of this thesis explores the potential application of the Fukui index in describing sites for charge transfer processes (donation and acceptance). A highly reactive site, as identified by this descriptor, indicates an atom that is prone to donate or receive electrons to/from the environment. This interpretation was applied to different donor and acceptor materials typically employed in organic solar cells, ranging from those considered the best in their category to others that have already been replaced by superior alternatives (WEI et al., 2020). The aim is to employ this descriptor to understand the molecular-level factors that contribute to efficient charge transfer processes.

The second chapter focuses on determining the chemical pathway from 1-azafulvenallene to phenylnitrene. Typically, such calculations involve the Intrinsic Reaction Coordinate (IRC) approach, known for its complexity and high computational demands. This chapter introduces the use of the local softness descriptor to explore intramolecular interactions, contrary to the conventional focus on intermolecular interactions. By doing so, it identifies potential pathways at a significantly reduced computational cost. Our goal is not to replace the IRC approach but to demonstrate the local softness descriptor's ability to identify viable pathways. The combination of both descriptors aims to achieve more accurate and expeditious results.

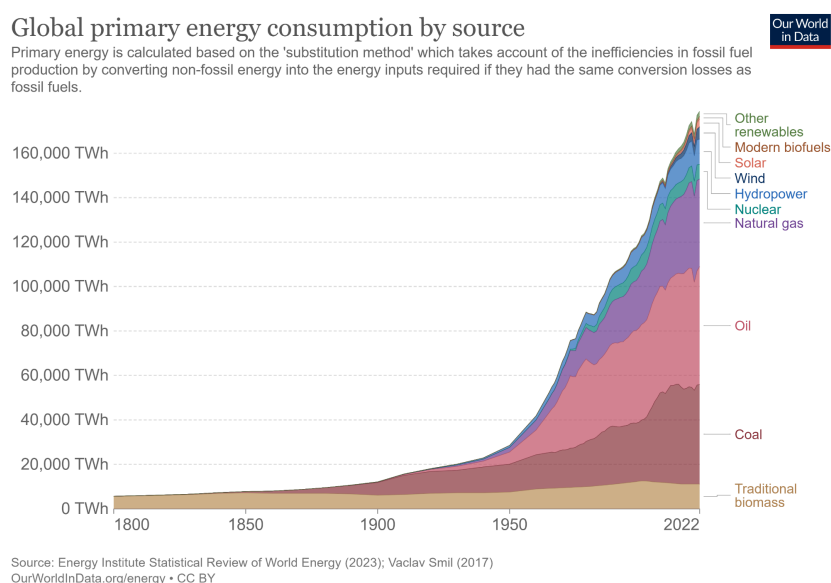
While the two chapters address distinct challenges, they share a common thread, utilizing the same reliable and computationally cheap tool. The overarching objective is to showcase the versatility of this tool and its potential to unravel material properties. Furthermore, it emphasizes the tool's compatibility with other methods to construct a more efficient approach.

1 NON-FULLERENE ACCEPTOR-BASED BULK HETEROJUNCTION ORGANIC SOLAR CELL THEORETICAL STUDY

1.1. INTRODUCTION

Since its inception in the 19th century, electricity has become an indispensable element of daily life. In the last 50 years, electricity consumption went from 72,000 TWh to nearly 180,000 TWh (RITCHIE, 2021). That is more than 100% in growth, which shows the undeniable human dependence on electricity. According to the International Energy Outlook 2021 (IEO), global energy consumption will increase by nearly 50%, mainly due to the industrial and transportation sectors of non-OECD (Organisation for Economic Co-operation and Development) countries' economic growth (NALLEY; LAROSE, 2021). It's clear that such an increase can cause harm to the environment, depending on the kind of energy sources that are going to be used, and although IEO projects that renewable sources will increase in use, so will petroleum and biofuels (NALLEY; LAROSE, 2021). Figure 1 shows a chart of the evolution of energy consumption over the past 200 years.

Figure 1.1. Global primary energy consumption by source from 1800 to 2022.

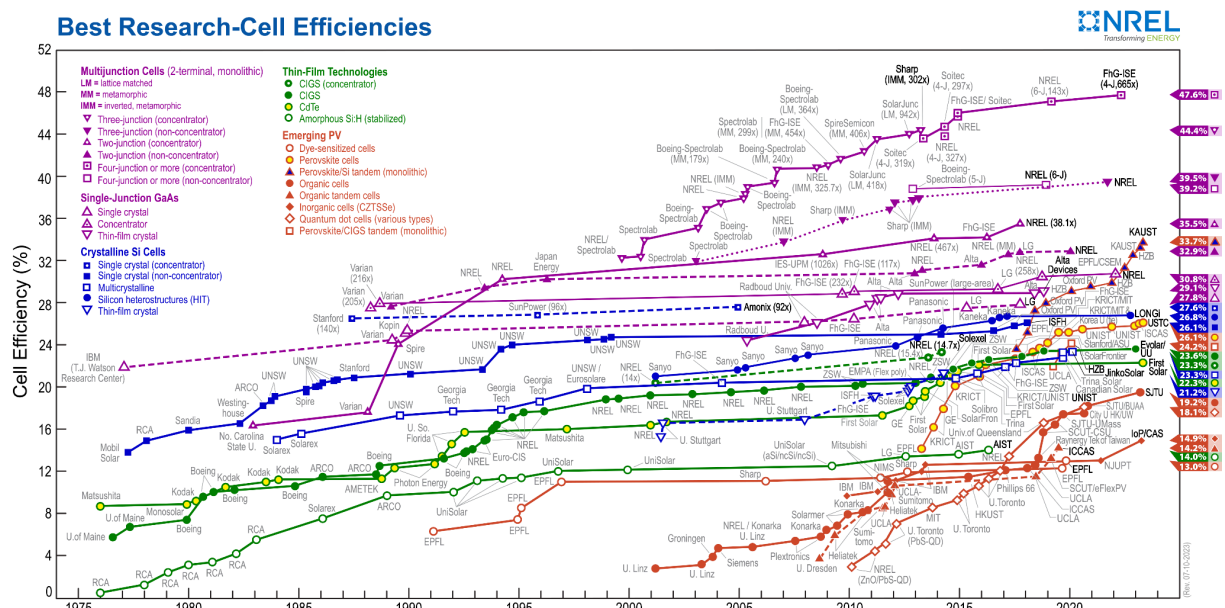


Source: Our World in Data - <https://ourworldindata.org/global-energy-200-years>

There is an earnest endeavor to put forth better and refined renewable energy alternatives. The tangible outcomes of this initiative are evident, as pictured in Figure 1.1: the utilization of oil, coal, and biomass had a significant decline from 80% to approximately 60% over fifty years. Furthermore, among the energy sources from the chart, IEO2021 envisions a noteworthy shift where solar energy will surpass coal as the predominant source of electricity by 2050 (NALLEY; LAROSE, 2021).

Among the solar energy alternatives, its conversion into electrical energy by means of solar cells deserves attention. These devices can be made from various materials, including but not limited to crystalline Si, single-crystal GaAs, perovskite, quantum dots, and organic cells (AJAYAN et al., 2020; KNECHTLI; LOO; KAMATH, 1984; SELOPAL et al., 2020; WEI et al., 2020). The National Renewable Energy Laboratory (NREL) provides an updated chart with the newest technology in solar cells and their record power conversion efficiency (PCE). Figure 1.2 shows this data.

Figure 1.2. Best Research-Cell Efficiencies.



Source: NREL website - <https://www.nrel.gov/pv/cell-efficiency.html>

Note that there is a category of cells, called Emerging PV, where the organic solar cells (OSCs) are present. They received this name due to the use of organic materials, such as polymers and small molecules, in their active layer. The late 80s saw the pioneering of this category of solar cells (TANG, 1986), which rapidly evolved. They are of considerable

interest due to their advantages, including, but not limited to, relatively low cost, flexibility, synthesis versatility, and lightweight (LU et al., 2021).

Generally, at their bare minimum, these devices consist of an anode, a cathode, and an active layer between them. The electrical conversion takes place via charge transfer (CT) processes between the active layer components, a donor (D) and an acceptor (A) material. In brief, the active layer will absorb a photon and use its energy to move an electron from the valence band to the conduction one. Upon such a phenomenon, the valence band hosts a quasiparticle called a hole. This entity has a charge with the same magnitude as the electron but is positive. The proximity between negative and positive charges generates a bounded electron-hole pair, called an exciton, a neutral quasiparticle. The exciton moves through the material and dissociates at the D/A interface. After dissociation, the electron is transferred to the acceptor molecules, while the hole remains in the D. This is called a CT state, which might require different amounts of energy to dissociate (typically around 0.3 eV in organic compounds - called exciton binding energy). Once dissociated, the charge carriers are permanently separated. These carriers move along the A and D domains and are collected on the electrodes. Electrons are collected on the cathode, and holes on the anode, constitute the electrical current (SHOAEE et al., 2023).

Initial iterations of OSCs exhibited notably low PCE, registering at less than 1%, a stark contrast to the recent advancements where efficiencies of approximately 20% have been attained (LIU et al., 2020; MOREL et al., 1978; ZHENG et al., 2022). Achieving such a high PCE required multiple steps undertaken over years of research. Arguably, a crucial advancement was achieved using a blend of D and A materials in the active layer, defining the so-called bulk heterojunction solar cells (BHJSC) (YU et al., 1995). The increase of D-A interfacial area improved the exciton dissociation, enabling the generation of a greater number of free charge carriers (electrons and holes) and higher PCE cells.

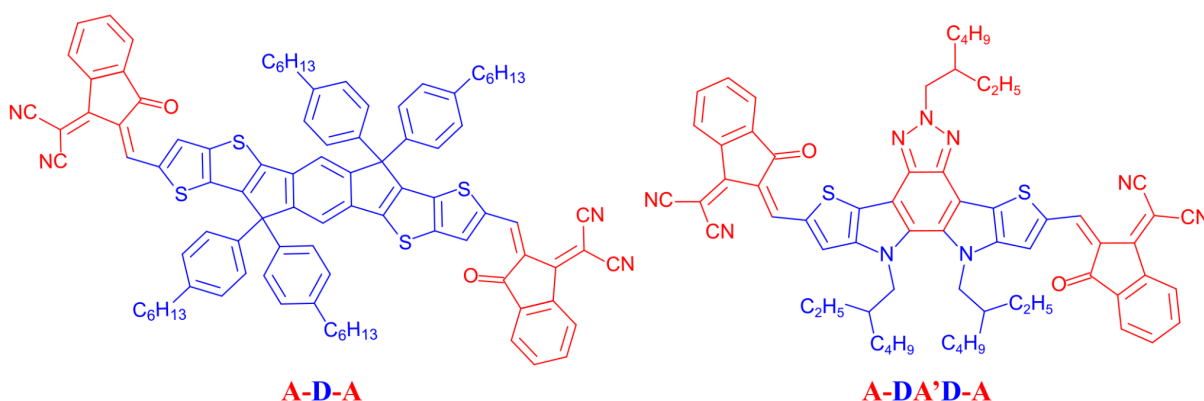
Initially, the constituents of BHJSCs typically consisted of wide-bandgap polymers as donors (D) and fullerene-based materials as acceptors (A). This paradigm leads the PCEs by around 8% (XIAO et al., 2016). However, although a significant enhancement to OSC, these new BHJSCs had a significant issue, associated with the intrinsic low light absorption capability of the devices, that limits the PCE (LIU et al., 2020). Naturally, the typical low optical absorption of fullerene derivatives pointed out that new classes of materials should be used as A to hinder this deficiency. Nowadays, the BHJSC active layer consists of a D polymer and a small molecule acceptor (SMA) with a narrow electronic gap (SHOAEE et al., 2023). These new SMAs were not spherical like the fullerenes-base materials and had

anisotropic charge transfer, which required them to be carefully matched with a proper donor to achieve the desired results (SHOAE et al., 2023).

A classic D that could universally match many fullerenes and SMAs was the PBDB-T (poly[[4,8-bis[5-(2-ethylhexyl)-2-thienyl]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]-2,5-thiophenediyl[5,7-bis(2-ethylhexyl)-4,8-dioxo-4H,8H-benzo[1,2-c:4,5-c']dithiophene-1,3-diyl]]) series, a copolymer with both D and A building blocks. This material had improved structural properties, producing devices with high fill factors (FF) and lower energy losses (SHOAE et al., 2023). Nowadays, highly efficient OSCs are made of PBDB-T-based polymers, such as PBTT-F, PM6 (PBDB-T-2F), PM7 (PBDB-T-2Cl), and D18 (CHAO et al., 2020; CUI et al., 2020; LIU et al., 2020; MA et al., 2020; WEI et al., 2020). As these polymers are derived from the same structure (PBDB-T) with small changes, and for the sake of simplicity, only their common names will be employed in this text (e.g. abbreviations).

Regarding the active layer, SMAs experienced substantial design improvements to achieve A materials that are suitable pairs for the previously mentioned D polymers. One of the first suitable SMA was benzotriazole. However, advancements in the field suggested the relevance of donor blocks integration in SMAs, building the A-D-A type materials (SHOAE et al., 2023). Optimizing the A-D-A structure was a gradual process. Alkyl side chains addition, D unit optimization, and, eventually, the change of D block into a DA'D backbone (e.g. BZTP - dithieno[3,2-b]pyrrolobenzotriazole) as the central unit can be cited as illustrative examples of design alternatives to achieve more efficient acceptors. Then, Zou et al. implemented BZTP in the A-D-A type SMA, turning it into an A-DA'D-A acceptor (SHOAE et al., 2023). The A' stands for an electron-deficient acceptor subunit into the central D core. The final step that leads to the more recent materials was proposed by Feng *et al.* whose used 2-(3-oxo-2,3-dihydroinden-1-ylidene) as the A units at the edge of the dithieno[3,2-b]pyrrolobenzotriazole (BZTP) core, introducing the non-fullerene acceptor (NFA) BZIC in 2017 (FENG et al., 2017). Figure 1.3 brings a schematic representation of these structures.

Figure 1.3. Examples of A-D-A and A-DA'D-A molecules.



Source: Author.

The development of enhanced NFAs continued, applying a variety of chemical modifications to both the DA'D core and the A side groups. A remarkable step was the use of benzothiadiazole core-based NFAs, presented in the Y-series and BZTP-series (SHOAEE et al., 2023; WEI et al., 2020). Although new enhanced NFA-based devices keep appearing, Y6 (and similar) NFAs are now considered the pinnacle of OSC (WEI et al., 2020).

Wei and collaborators have compiled a set of information regarding the best performing NFA for OSC, showing that PM6:Y6 combination (or their variations) always presents relevant characteristics such as high FF, open circuit voltage (V_{oc}), short circuit current (J_{sc}), and PCE (WEI et al., 2020). However, it is not clear why NFAs are so much better than fullerene-based acceptors. Although great studies, for instance, the recently published "What have we learnt from PM6:Y6" by Shoaee and collaborators, tackle some topics regarding the superiority of Y6, there are still many other aspects to debate and investigate (SHOAEE et al., 2023). Inspired by the works of Yuan and Zou, Qiu and Zheng, and Lu and collaborators, this work set out to explore the relevant properties of OSC materials. This investigation was conducted at the molecular level, employing electronic structure-based calculations (LU et al., 2021; QIU; ZHENG, 2021; YUAN; ZOU, 2022).

In brief, this study seeks to identify some molecular features of D and A that are desirable to build an efficient D:A pair for OSC application. To achieve this goal, several D:A pairs were investigated. The famous Y6 acceptor was the core of this study, given its position as one of the best NFAs. The second backbone of this theme is the polymers PM6 and D18, common pairs of Y6 in the OSC active layer. With these materials, the highly efficient pairs PM6:Y6 and D18:Y6 can be investigated. Moreover, the onset of A-DA'D-A NFA-based OSC, the HFQx-T:BZIC, and the pre-NFA OSC pair, P3HT:PCBM, were also evaluated for

comparison purposes. These two pairs are regarded as inefficient and outdated ones, however, their study allows a relevant comparative analysis to trace the properties of interest.

As a matter of fact, comparative studies involving different A:D systems can provide valuable insights into their fundamental properties and contribute to the development of new, optimized combinations. In this context, molecular modeling studies serve as essential tools, enabling the calculation and analysis of a wide range of properties. In particular, our group has been using reactivity electronic descriptors, such as condensed-to-atoms Fukui indexes (CAFI), to study a great diversity of organic materials for distinct applications (BARBOZA; GOMES; BATAGIN-NETO, 2021; CUBA et al., 2021; G. B. ALVES; BATAGIN-NETO, 2023; GALINDO et al., 2020; MAIA; VENTORIM; BATAGIN-NETO, 2019). Recent studies have proven the potential of using such descriptors to investigate materials for OSC applications (DOAT et al., 2022; FREITAS et al., 2024), mainly due to its interpretation as charge transfer descriptors which allow the identification of acceptor and donor molecular sites (DE PROFT et al., 2002; DOAT et al., 2022; LEWARS, 2016). Moreover, the CAFI precursor, the Fukui function, has been modified and applied to study the CT process in a dimeric system (KORCHOWIEC; UCHIMARU, 1998), leading to the charge transfer Fukui indexes (CTFI). The advantage of CTFI over CAFI is the capability to properly indicate relevant CT sites for dimeric systems. It's believed that using CAFI and CTFI, alongside other molecular-level property studies, might lead to insightful results about NFA and OSC. Furthermore, to better assess the capabilities of donating and accepting electrons quantitatively, two complementary approaches were also used in this thesis: i) the evaluation of donor-acceptor maps (DAM) (MARTÍNEZ et al., 2008) and ii) the estimation of local electron donating and accepting powers (LEDAP) (GÁZQUEZ; CEDILLO; VELA, 2007). DAM analysis offers a global comparison between the systems' electron accepting and electron donation capabilities, while LEDAP shows how these capabilities are distributed on the atoms.

In summary, this chapter evaluates four different D:A pairs (D18:Y6, PM6:Y6, HFQx-T:BZIC, and P3HT:PCBM), seeking a better understanding of which properties are responsible for highly efficient OSC. Individual molecule CAFI studies showed different site accessibility for electrons and holes, depending on the material, and allowed for discussing plausible CT routes. In particular, Y6 CT routes were further explored by CTFI studies, considering Y6 dimers in five different stacking conformations. The Y6's ambivalent CT network was observed at the molecular level through this methodology. The LEDAP and DAM studies the definition of an acceptance and donation ranking among the materials, by

considering simple to calculate descriptors: *i*) Donors - D18 >>PM6~HFQx-T>>P3HT; *ii*) Acceptors - Y6>BZIC>>PCBM. More specifically, DAM results allowed us to propose an additional parameter besides complementary wavelength absorption when choosing donor and acceptor materials for OSC.

Overall, the descriptors were able to identify relevant CT processes, tying molecular-level results to observed experimental phenomena. The developed CTFI showed in greater detail how CT processes happen in a crystal/stacked structure. These findings highlight how low-cost molecular descriptors can effectively predict charge transfer sites and guide material selection for organic solar cells.

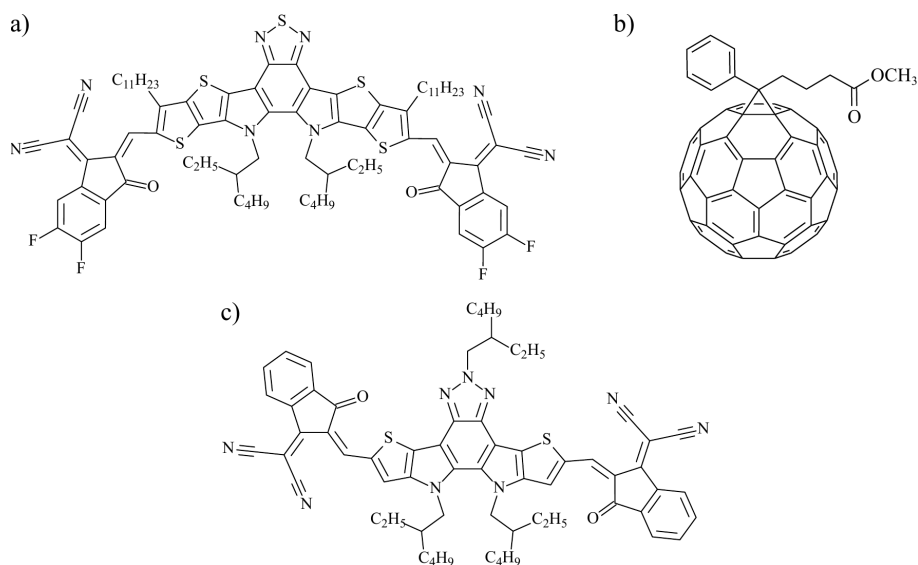
1.2. MATERIALS AND METHODOLOGY

This section is divided into two main sections: *i*) Materials, where the molecules and chemical structures evaluated in the chapter are presented, and *ii*) methodology, where the basic parameters of the used techniques are described without much deeper discussion about their theory or development. Additional details regarding some descriptors and techniques are presented in the Appendixes. However, further and deeper explanations about the theories can be found in reference books (JENSEN, 2017; LEWARS, 2016; PARR; YANG, 1994).

1.2.1. MATERIALS

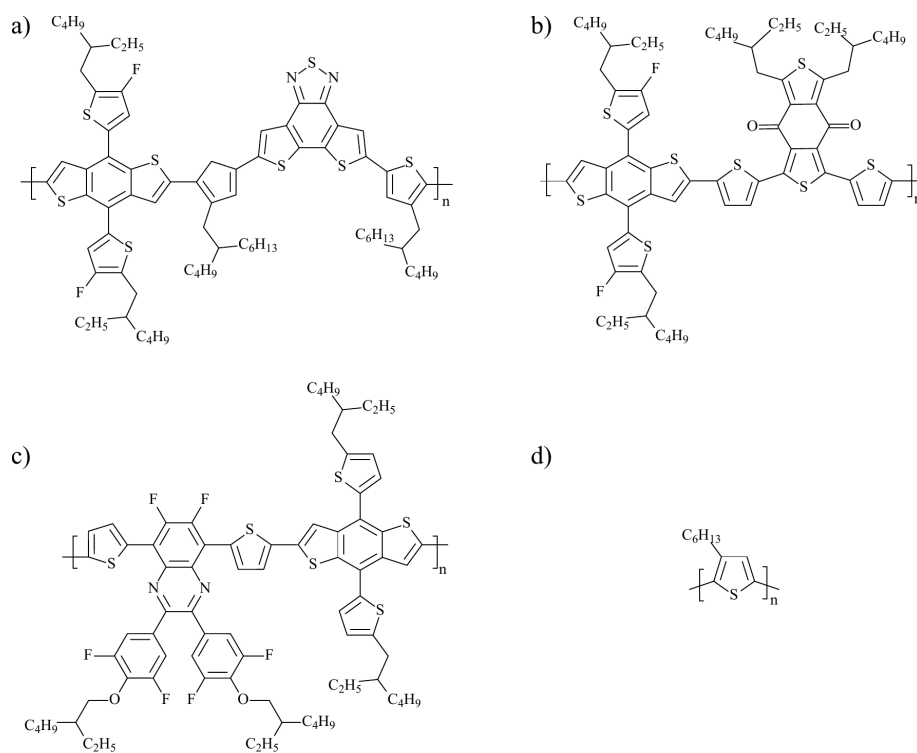
Seven different materials were selected for this study: high PCE NFA-based pairs (D18:Y6 and PM6:Y6), the first NFA-based pair (HFQx-T:BZIC), and a traditional fullerene-based pair (P3HT:PCBM). The chemical structures of the three A materials, and the four D materials are presented in Figures 1.4 and 1.5, respectively.

Figure 1.4. Acceptor materials: a) Y6, b) PCBM, and c) BZIC.



Source: Author.

Figure 1.5. Donor materials: a) D18, b) PM6, c) HFQx-T and d) P3HT.



Source: Author.

1.2.2. METHODOLOGY

Many different techniques and methodologies were employed in this study. Some theoretical or technical details might be skipped along this section, however, they ought to be found in their specific appendix.

1.2.2.1. STRUCTURE DESIGN AND OPTIMIZATION

Usually, when designing a molecule, a common practice is to use 3D software. For such, a variety of freely available options, adapting effectively to a wide range of applications, can be found. While suitable for most purposes, these tools may encounter limitations. Building highly fused planar molecules like the NFAs can be particularly challenging, often requiring more time than anticipated.

The molecules Y6, PM6, D18, HFQx-T, and BZIC were first drawn as 2D chemical structures using the KingDraw software, the geometries were saved as “.mol” extension (KINGDRAW, 2019). This extension allows the opening of these 2D structures in 3D software. The next step was to open such files using Avogadro software with the option to convert them to 3D structures (HANWELL et al., 2012). After the conversion, some adjustments in bond lengths and dihedral angles were made to get a better initial structure, made with the aid of Molden software (SCHAFTENAAR; NOORDIK, 2000). Regarding the remaining structures, P3HT was directly designed on Molden, while PCBM was designed with the aid of the Gabedit computational package (ALLOUCHE, 2011; SCHAFTENAAR; NOORDIK, 2000).

The calculations were made considering a DFT framework (see Appendix A), a common choice for this kind of organic material simulations, being conducted with the aid of Gaussian 16 software (FRISCH et al., 2016; QIU; ZHENG, 2021; SHOAEE et al., 2023; XIANG; XU; ZHENG, 2023; ZHANG et al., 2020). The first step is defining which basis set and exchange-correlation (XC) functional to use (more on XC functionals and basis set can be found in Appendix B and C, respectively), which is a considerable task. Throughout this investigation, a critical aspect involves comparing various materials. Thus, applying the same framework consistently across all of them is necessary. Beyond being a reasonably good functional to all materials, one must be aware of the computational cost, especially considering some targets are polymers of 100-plus atoms monomers. Using the most accurate, comprehensive, and computationally demanding functional/basis set is not a feasible option.

At last, the chosen framework must primarily be an optimal fit for Y6, as it's the backbone material for this study.

In recent reports, it has been noticed that ω -B97x/-D is a popular choice of an XC functional. It exhibits long-range and atom-atom corrections with tunable ω parameter and is considered a good choice for Y6 and derivatives (CHAI; HEAD-GORDON, 2008; KUPGAN; CHEN; BRÉDAS, 2021; QIU; ZHENG, 2021; SHOAEE et al., 2023; XIANG; XU; ZHENG, 2023; ZHANG et al., 2020). Conversely, the use of such a powerful functional comes with a high computational cost. To test how expensive the use of ω -B97x/-D would be, a PM6 monomer was fully optimized with B3LYP (BECKE, 1993; LEE; YANG; PARR, 1988) and then this structure was re-optimized considering ω -B97x/-D functional (using the same basis set), the latter optimization took ten times longer than the first. Moreover, it is imperative that all polymers be saturated (i.e. presenting an appropriate balance between oligomer size and reproduction of basic polymer electronic properties), signifying their progressive increase in size and complexity. It is unfeasible to use ω -B97x/-D for such complex systems. Considering the complete set of circumstances, the use of B3LYP has proven to be the optimal choice. Such an XC functional is relatively cheap and offers reliable results for a myriad of organic materials including NFAs and typical donors, as shown by our group's works (BARBOZA; GOMES; BATAGIN-NETO, 2021; G. B. ALVES; BATAGIN-NETO, 2023; GALINDO et al., 2020) and others (CHAI; HEAD-GORDON, 2008; CUI et al., 2020; GONG et al., 2021; MAKKAR; GHOSH, 2021; QIU; ZHENG, 2021; XIANG; XU; ZHENG, 2023).

A more straightforward decision was in determining the appropriate basis set to use. Even for ω -B97x/-D functional, the 6-31G (with or without polarization and diffusion) was the better choice (QIU; ZHENG, 2021; SHOAEE et al., 2023; XIANG; XU; ZHENG, 2023; ZHANG et al., 2020). In short, 6-31G with the polarization functions (d,p) was chosen for a better electron description. Given all the considerations presented above, our computational framework can be expressed as DFT/B3LYP/6-31G(d,p).

The described process is sufficient to advance to properties calculations with acceptor materials. Conversely, the donor polymers require a saturation study. For both classes of materials, alkyl side chains are modified to methyl ramification, as both have similar effects on the electronic properties, with the latter being much simpler (BATAGIN-NETO et al., 2013; GALINDO et al., 2020).

1.2.2.2. SATURATION STUDY FOR POLYMERS

As mentioned, this work is mainly concerned with the molecular scale properties, which might sound antagonistic to half of our materials, the D polymers. The reason is that polymers are, in simple terms, an infinite chain of repeating units (monomers). Working effectively with molecular scale properties of a seemingly infinitely long material requires some adjustments. One way to achieve this is what is called saturation of selected optoelectronic properties.

To saturate the properties, it is necessary to grow a polymer, monomer by monomer, and observe their properties evolution. At some point, such properties will not change significantly, and at this moment, we have a saturated n -oligomer. One property to observe is the frontier molecular orbital (FMO) energy, that is, grow your polymer until the energy difference between the last two sizes (n and $n-1$) is no greater than the environment's available thermal energy ($kT=0.025$ eV). This energy limit relates to what is observed in nature.

Another well-reported saturation approach is based on Meier's fit method, which has been proven successful and used for a set of polymers and other conjugated systems (COLEONE; BARBOZA; BATAGIN-NETO, 2021; COLEONE; LASCANE; BATAGIN-NETO, 2019; GAO et al., 2025; GIERSCHNER; CORNIL; EGELHAAF, 2007; HUANG et al., 2025; IWATA; TSUJI, 2025; KARSTEN et al., 2008; ROMI et al., 2024). This method involves observing the evolution of the absorption main peak position with the number of added units. These observed points are then fitted by an exponential equation as proposed by Meier *et al.* (MEIER; STALMACH; KOLSHORN, 1997):

$$\lambda(n) = \lambda_{\infty} - \Delta\lambda \exp[-a(n-1)], \quad (1.1)$$

where n refers to the number of monomers; λ_{∞} is the absorption main peak position for $n \rightarrow \infty$, that is, in the polymer form; and $\Delta\lambda = \lambda_{\infty} - \lambda_1$, where λ_1 is the absorption main peak position for the monomer ($n=1$). The a parameter is the indicator of how fast the limit of convergence is achieved.

The idea proposed by Meier *et al.* is that one might evaluate the effective oligomer size, n_{ef} , assuming a detection limit for wavelength variation of ~ 1 nm (commonly noticed in most of the commercial spectrometers), so that:

$$\lambda_{\infty} - \lambda_{ef} \leq 1nm, \quad (1.2)$$

where λ_{ef} is the absorption peak for a n_{ef} sized oligomer. That means, by considering an oligomeric system with this size it is possible to simulate essential features of the optical properties of the polymer.

To use Meier's approach, it is necessary to calculate the absorption peak of a series of oligomeric structures with distinct sizes. This calculation can be performed in a variety of ways. More specifically, in the DFT framework, a study by Oliveira *et al.* (2016) proposes a route of calculations to obtain reliable light absorption results in polymers. The strategy is to use the XC functional M06HF (ZHAO; TRUHLAR, 2006) for optimization, followed by the time-dependent DFT (TD-DFT) light absorption calculations using B3LYP (OLIVEIRA *et al.*, 2016). For more information on light absorption calculation and TD-DFT see Section 1.2.2.4 and Appendix F.

The optimization in a M06HF framework can be rather demanding. To reduce such demand, a good initial structure is suggested. Therefore, a pre-optimization with B3LYP is done before the M06HF one. These B3LYP-optimized polymers are then used for MEP and CAFI calculations. In short, the general strategy incorporated for saturation studies is to start from a monomer, optimize in a DFT/B3LYP/6-31G(d,p) framework, and obtain its FMO energy data. Followed by another optimization changing the XC functional to M06HF, and then the light absorption calculation in the TD-DFT/B3LYP/6-31G(d,p) framework. These steps are then repeated as the monomer grows to longer oligomers. Moreover, as the FMO energy results are much quicker, it was used to guide how far Meier's approach should advance.

A noticeable issue when growing oligomeric systems is how the units connect with other units. The dihedral angle between units dictates the polymer planarity and its stability. In this sense, each polymer requires a between-units dihedral angle study to verify these connections.

In general, this process is simple. Usually, it requires scanning various dihedral angle values with single-point calculations (without geometry relaxation) to find the lowest energy one. The most concerning problem faced at this step is the computational time. Besides P3HT, the studied polymers have large and intricate monomers (around 100 atoms each). Such structures reached the practicality limit at five repeating units (pentamer, 5mer) using M06HF functional for optimization. This problem aggravates for HFQx-T due to its intricate structure with multiple rotating rings. To overcome this problem, the monomer was split into two halves, and each relevant dihedral angle was calculated and saved for further calculations (see Appendix H for more details).

1.2.2.3. REACTIVITY STUDIES

Different methods can evaluate a molecule's reactivity. In this work, CAFI was used as the reactivity electronic descriptor (LEWARS, 2016; YANG; MORTIER, 1986). This index describes how much an atom's electronic density changes when the total number of electrons in the system changes (from neutral to cationic or anionic configurations) (DE PROFT et al., 2002). It enables the evaluation of local propensities for electron removal or acceptance within the molecule, identifying which sites are prone to react with nucleophilic agents, electrophilic agents, or free radicals (LEWARS, 2016).

Regardless of CAFI's simplistic approach, researchers have successfully applied CAFI for the study of various molecules and polymers for different applications (BARBOZA; GOMES; BATAGIN-NETO, 2021; COLEONE; BARBOZA; BATAGIN-NETO, 2021; G. B. ALVES; BATAGIN-NETO, 2023; GALINDO et al., 2023; LIMA et al., 2021). As mentioned, CAFI identifies tendencies for three types of interactions:

$$f_k^+ = p_k(N_0 + 1) - p_k(N_0) \quad (1.3)$$

$$f_k^- = p_k(N_0) - p_k(N_0 - 1) \quad (1.4)$$

$$f_k^0 = \frac{1}{2} [p_k(N_0 + 1) - p_k(N_0 - 1)] \quad (1.5)$$

These equations calculate the molecule local reactivity towards distinct external species: nucleophilic agents (Eq. 1.3), electrophilic agents (Eq. 1.4) and free radicals (Eq. 1.5). In the equations, p_k represents the electronic population of the k -th atom as a function of the number of electrons in the system ($p_k(N)$). N_0 is the total number of electrons in the molecule in its neutral state, therefore N_0+1 represents an anionic system, and N_0-1 a cationic one. Notice that each f_k^n has to be calculated for every atom in the molecule, indicated by k .

As can be seen, to calculate the indexes, the only requirement is obtaining the electronic population on each atom in three scenarios: neutral, cationic, and anionic molecular states. These values are obtained from Kohn-Sham orbitals' iterative calculations without geometry optimization (also known as single point calculations), considering a previously optimized structure with N_0 electrons. CAFIs were also estimated in a DFT/B3LYP/6-31G(d,p) approach, with the aid of Gaussian 16 computational package, thus keeping a consistent method (FRISCH et al., 2016). When calculating the electronic population, there are many charge partitioning methods that lead to different results. Our choice was the use of Hirshfeld (or stockholder) partitioning charge method. Such method has been reported as the most suitable method for CAFI calculation, since it avoids possible negative reactivity values (HIRSHFELD, 1977; RITCHIE, 1985; RITCHIE; BACHRACH,

1987; ROY; PAL; HIRAO, 1999). More details regarding reactivity descriptors and charge partitioning methods can be found in Appendices D and E.

The CAFI calculation inputs are just atomic electron populations that are added or subtracted to obtain the reactivity indexes. Therefore, to have more appealing results and facilitate the analysis, a specific homemade Fortran and Bash hybrid routine was used to calculate the reactivity and associate it with an RGB scale. This routine writes that information in a Jmol script format so that this software can produce colored pictures (JMOL, 2010).

1.2.2.4. OPTICAL ABSORPTION CALCULATIONS

Section 1.2.2.1 showed that optical absorption calculations are fundamental to conduct an appropriated polymer saturation study. The optical process comes from light-matter interaction when matter (electrons) absorbs energy from light (photons), leading to an electronic excited state (EES). This phenomenon is time-dependent due to the nature of electromagnetic waves (ADAMO; JACQUEMIN, 2013). Hence, regular DFT is not able to compute it, a time-dependent DFT approach is required (TD-DFT), which was formalized by Runge and Gross thirty years ago (ADAMO; JACQUEMIN, 2013; CASIDA, 1995; RUNGE; GROSS, 1984). Notice that alternative approaches to TD-DFT exist. However, they either offer lower accuracy (Hartree-Fock ZINDO-based Hamiltonian, among others) or require significant computational resources (highly correlated *ab initio* methods) (JACQUEMIN; MENNUCCI; ADAMO, 2011).

Since its debut, TD-DFT has been successfully applied for varied systems and has evolved much. However, the dependence between its reliability and the XC functional of choice is still an issue (JACQUEMIN; MENNUCCI; ADAMO, 2011). In this context, applying the B3LYP XC functional ensures consistency with previously made calculations. Thankfully, the benchmark study from Adamo and collaborators shows that it is among the best options, presenting below-average mean signed and mean absolute error for a series of organic materials (JACQUEMIN; MENNUCCI; ADAMO, 2011).

In this work, TD-DFT-based calculations were used to estimate the first state absorption peak (for polymer saturation studies). However, it's capable of much more, such as calculating EES optimal geometry, vibrational frequencies, vibronic coupling, dipole moment, and atomic point charges (ADAMO; JACQUEMIN, 2013). Appendix F brings more details about TD-DFT equations and development.

In this thesis, the same framework was applied for DFT and TD-DFT calculations (B3LYP/6-31G(d,p)), as implemented in Gaussian 16 (FRISCH et al., 2016). TD-DFT calculations were conducted only for singlet excited states of one electron, requesting only the first five transitions.

1.2.2.5. MOLECULAR ELECTROSTATIC POTENTIAL CALCULATION

The interaction and reaction between molecules, or even charge and molecules, can be studied by the CAFI, as stated previously. Although not specified, CAFI has a distance dependency, reminiscent of the Fukui function and molecular overlap (see Appendix D). At distances out of its domains, these interactions and reactions are dominated by electrostatic interactions.

One approach to study such long range intermolecular interactions is considering the molecular electrostatic potential (MEP). Using a DFT/B3LYP/6-31G(d,p) approach and with the aid of Gaussian 16 software (or similar), it's possible to calculate the MEP through the molecule's charge distribution. For a reliable calculation, the specific charge partitioning method called CHelp scheme was used (CHIRLIAN; FRANCL, 1987).

This charge partitioning scheme makes an adequate calculation of the MEP, allowing for reliable results. Similarly to CAFI, Jmol software was also used to produce the figures. The MEP analysis allows us to estimate the electronic distribution around the molecules, and then identify (more/less) positively and negatively charged portions on the structures.

1.2.2.6. CHARGE TRANSFER FUKUI INDEXES

In Section 1.2.2.3 it defines the local reactivity indexes mainly used throughout this work, the CAFI. One speculation that emerges when using these descriptors is how reliable CAFI are to indicate CT sites. CAFI's theoretical interpretation allows us to identify which sites are prone to act as D and A centers in the molecules, and they can be estimated from HOMO and LUMO spatial distribution (FUKUI; YONEZAWA; SHINGU, 1952; LEWARS, 2016; PARR; YANG, 1994). Therefore, it is possible to think that CAFI could, at least, give hints about CT processes

In this sense, in 1998, Korchowiec and Uchimarú published an article tackling molecule interaction with CT using Fukui functions and presenting their equations in terms of electronic density and atomic resolution (KORCHOWIEC; UCHIMARU, 1998). For a system of two interacting molecules, there are two CTFIs, one for each molecule's point of view.

Four components must be calculated to obtain these two CTFI. Considering a system composed of molecules A and B, these components are:

$$f_{AAk} = p_{Ak}(N_A + 1, N_B) - p_{Ak}(N_A, N_B) \quad (1.6a)$$

$$f_{BAk} = p_{Ak}(N_A, N_B) - p_{Ak}(N_A, N_B - 1) \quad (1.6b)$$

$$f_{ABk} = p_{Bk}(N_A + 1, N_B) - p_{Bk}(N_A, N_B) \quad (1.6c)$$

$$f_{BBk} = p_{Bk}(N_A, N_B) - p_{Bk}(N_A, N_B - 1) \quad (1.6d)$$

Similarly to CAFI, p_k represents electron populations on atom k , however here it happens for both molecules (A and B), and N_A and N_B are the total number of electrons for A and B, respectively. However, when calculating p_{Ak} (p_{Bk}), molecule B (A) is not present, only its atomic charges are used in a point charge representation. This consideration makes it possible to add or remove electrons from just A or B.

In relation to CAFI, there are many similarities to be commented on. First, (1.6a) is basically the equation for f^+ happening for A while B remains neutral. On the other hand, (1.6d) is f^- , happening for B while A remains neutral. Then it is possible to see that (1.6b) is (1.6d) but calculated in the point of view of A, and (1.6c) is just (1.6a) in B's point of view.

The indexes f_{AA} (f_{BB}) are of pretty straightforward interpretation, they show which sites in A (B) are prone to interact with nucleophilic (electrophilic) agents, respectively, while in presence of B (A) charge distribution. These are called diagonal components by Korchowiec and Uchimaru (KORCHOWIEC; UCHIMARU, 1998).

The other two indexes are the off-diagonal ones, as mentioned they present the same calculations from the other two but from the opposite molecule's point of view, *i.e.* if the change in charge happens in A, it shows the effect in B. For that reason it could be interpreted as an inductive effect. However, there is not a simple and direct interpretation for them, not that it is necessary, given that all four indices' purpose is building the CTFI itself.

Using Equations (1.6a) to (1.6d), the CTFI can be calculated from the difference between the diagonal and off-diagonal components of each molecule:

$$f_{Ak}^{CT} = f_{AAk} - f_{BAk} = p_{Ak}(N_A + 1, N_B) - 2p_{Ak}(N_A, N_B) + p_{Ak}(N_A, N_B - 1) \quad (1.7a)$$

$$f_{Bk}^{CT} = f_{BBk} - f_{ABk} = p_{Bk}(N_A + 1, N_B) - 2p_{Bk}(N_A, N_B) + p_{Bk}(N_A, N_B - 1) \quad (1.7b)$$

In this set of equations it is considered that B loses an electron to the medium and becomes neutral, on the other hand A goes from neutral configuration to anionic state (or the other way around), it's called a two-step process. This consideration implies the existence of some kind of charge reservoir, *i.e.* something capable of receiving and donating electrons

without requiring extra energy ($B \rightarrow \text{reservoir}$ and $\text{reservoir} \rightarrow A$). It is in line to how CT processes can take place in an OSC device.

Another possibility is that the direct electron flow from B to A ($B \rightarrow A$), a 1-step process. In this case, that way of calculating CTFI is independent of the previous four indexes:

$$f_{Ak}^{CT} = p_{Ak}(N_A + 1, N_B - 1) - p_{Ak}(N_A, N_B) \quad (1.8a)$$

$$f_{Bk}^{CT} = p_{Bk}(N_A + 1, N_B - 1) - p_{Bk}(N_A, N_B) \quad (1.8b)$$

It is relevant to highlight that, for the CTFI, the system is always at zero net charge. At the starting point, both molecules are neutral. On the other hand, the endpoint has molecules with net charges +1 and -1, totalizing zero net charge. Both equation sets (1.7) and (1.8) can be equally valuable, as each might bring distinct interpretations. For instance, at first sight, Eq. (1.7) appears more generic since the electrons flow in and out of a reservoir. Therefore, these CT sites show how the molecule interacts with the environment (intersystem process) while in the presence of another molecule. Conversely, Eqs. (1.8) could be seen as more contained in the system, a kind of intrasystem CT process.

In short, highly reactive sites calculated by Eqs. (1.7) indicate where charges can enter from or leave to the outside, while the ones calculated by Eqs. (1.8) show how charges are transferred within the system, from A to B.

In section 1.2.2.3 it is made clear that CAFI are simple to obtain, requiring just three single-point calculations (no additional geometry optimization needed). CTFI are somewhat similar as just single-point calculations are necessary (based on a pre-optimized system). However, they require additional calculations. In this section, the wording “point of view” appears multiple times, it means that every calculation for molecule A needs to have molecule B represented, and vice versa. A possible solution to consider the presence of B around A is the use of external point charges (simulating the partial atomic charges on B) at the vicinity of A. It was done via Gaussian 16 “charge” keyword, which allows the user to add background charges by writing a matrix of point charges after the geometric information of the molecule.

To calculate the CTFI it is necessary the evaluation of atomic populations of the following (dimeric) systems: neutral A and B, anionic A, and cationic B (in the presence of appropriate charge points - background charges). In short, four single-point calculations are needed to obtain these distributions. Then, this charge information has to be written in the specific files to build the correct inputs. For instance, to calculate the Eq. (1.6a), the single point of anionic A with a neutral B background charge and the single point of neutral A with a

neutral B background charge must be calculated. As usual, all CTFI calculations were made in the same framework as before, employing the Hirshfeld charge partitioning method to estimate the electronic populations (DE PROFT et al., 2002; HIRSHFELD, 1977; ROY; PAL; HIRAO, 1999).

Another challenge is building an appropriate AB system, known as a dimer or dimeric system. One good solution is to use previously published results associated with A-B relative alignment coming from solid-state calculations. This approach was used for the Y6 dimeric system. Moreover, these calculations require that the dimeric AB system be easily separated in A and B, to write the background charge matrix and the inputs. To ease these processes, bash scripts were developed and applied.

The final obstacle is gathering all the information and presenting it in a manner that is both comprehensible and easily analyzable. Our group has developed specific routines for this purpose for the CAFI. An updated version capable of generating comparable results for CTFI was required. The final CTFI script closely resembles CAFI, necessitating only minor modifications and adaptations.

In total, for one AB dimeric system CTFI analysis, twelve single-point calculations are necessary. First, four isolated calculations to obtain the charges used as background. Then, eight calculations for the indexes: Six for the 2-step CTFI, and two more for the 1-step CTFI. All calculations considered the same framework as CAFI (DFT/B3LYP/6-31G(d,p)) calculations for consistent comparison.

1.2.2.7. DONOR-ACCEPTOR MAP AND LOCAL ELECTRON DONATING AND ACCEPTING POWERS

Considering a quantitative approach that could allow for direct comparison between materials, two approaches were adopted, a global and a local analysis. The global characteristic comes from the donor-acceptor maps (DAM). The DAM are employed to classify the electron-donating (R_d) and electron-accepting (R_a) powers of each studied compound. R_d and R_a indexes are derived from the material electrophilicity, which is ultimately related to the ionization potential and electron affinity (see Appendix G for further details) (MARTÍNEZ et al., 2008). Due to its nature, low R_d (high R_a) values indicate a good donor (acceptor) material.

It is possible to scale the electrophilicity to the atoms, in a condensed approach, by simply multiplying it by the CAFI. By performing this procedure, a new index is obtained to

quantify the electron-donating or electron-accepting ability of a specific atom. These local properties are defined as:

$$\omega_k^+ = \omega^+ f_k^+ \quad (1.9)$$

$$\omega_k^{-*} = \frac{f_k^-}{\omega^-} \quad (1.10)$$

where ω^+ and ω^{-*} define the molecule's local electron-accepting and electron-donating powers, respectively. Notice that Eq. 1.10 uses the inverse of ω^- (see Appendix G) for analysis purposes, in such a way that high values of ω_k^+ and ω_k^{-*} represent high accepting and donating capabilities (GÁZQUEZ; CEDILLO; VELA, 2007). When using such an approach it is possible to conduct comparative analysis between distinct compounds by considering normalized color maps.

1.3. RESULTS AND DISCUSSIONS

1.3.1. Y6 STUDIES

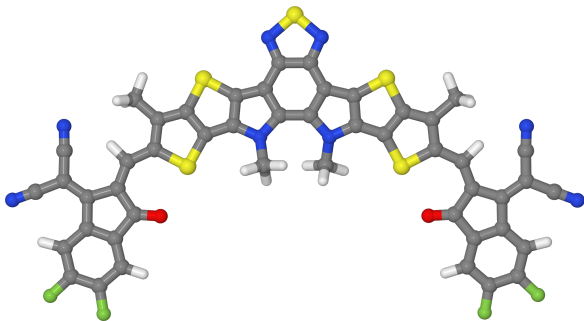
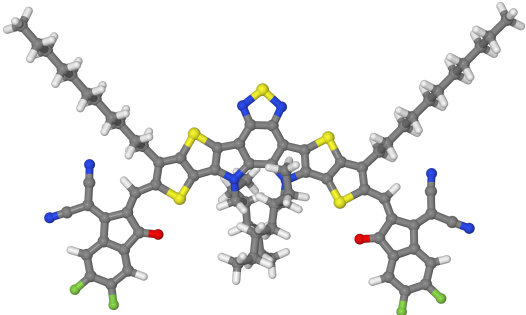
The A-DA'D-A NFA Y6 is considered the focus of this work, paired with its donors PM6 and D18 counterparts. Among many things, this work intends to compare other acceptors to Y6, considering this system as the model of the other ones.

1.3.1.1. STRUCTURAL STUDIES

The first step when working with a new molecule is to build it. Some molecules can be simple, but not Y6. This molecule is an A-DA'D-A NFA, which means it's composed of a "DA'D" core, one "A" end group (EG) on each side of the core, and alkyl side chains connected to the core, which makes its study quite complicated. To ease this process, the first Y6 structure produced had the side chains swapped for methyl, for simplicity. As mentioned in Section 1.2.2.1, a combination of Kingdraw and Molden software was used to build the first geometries of many of the studied molecules, followed by a conformational search process, and finally a full geometric optimization in a DFT/B3LYP/6-31G(d,p) framework.

Two Y6 variants were produced to assess the electronic relevance of extended side groups: i) one with all four alkyl groups and ii) another with only methyl groups. Table 1.1 shows the different optimized structures and their relevant energetic information (total energy, HOMO, LUMO, and the energy difference between the FMO energy level (ΔE_{LH})).

Table 1.1. 3D structure, total energy, FMO energy, and ΔE_{LH} for Y6 with and without side chains.

3D structure	Energy-related information (eV)	
	Total energy	-131121.324
	E_{HOMO}	-5.618
	E_{LUMO}	-3.575
	ΔE_{LH}	2.043
	Total energy	-167496.259
	E_{HOMO}	-5.544
	E_{LUMO}	-3.504
	ΔE_{LH}	2.040

Source: Author.

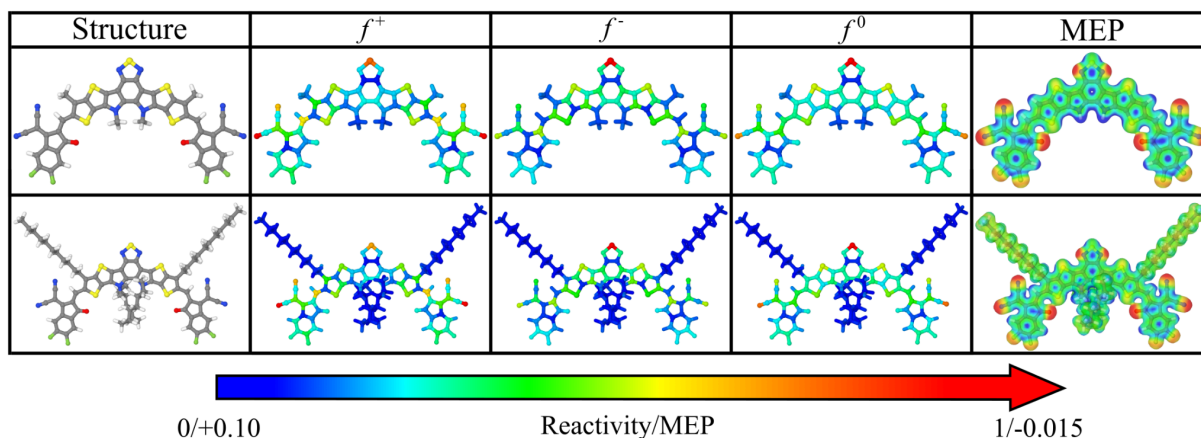
Obviously, the total energy has to be very different given the distinct number of atoms. Note that HOMO and LUMO energies are similar, with an offset of around 0.07 eV in opposite directions, leading to a difference of 0.003 eV in ΔE_{LH} . It's relevant to highlight that Y6 is basically a planar structure, with a small angle between the end group (EG) planes. Previously published studies and the NFAs' fused ring core pointed to these results (WEI et al., 2020; YUAN et al., 2019; YUAN; ZOU, 2022).

From previous studies of our group, it is known that alkyl has almost no effect on reactivity (the main focus of this work) (BATAGIN-NETO et al., 2013; GALINDO et al., 2020). However, the CFI study was also made for the complete Y6 to exemplify this effect (see Figure 1.6). Based on the obtained results, all the alkyl side chains in Y6 (and other materials) were replaced by single methyl groups in this study.

1.3.1.2. CAFI AND MEP RESULTS

Single-molecule CAFI and MEP were calculated for both forms of Y6, the results are shown in Figure 1.6. The RGB color scale arrow indicates the reactivity from CAFI (no units) and potential values for MEP (atomic units).

Figure 1.6. CAFI and MEP results for complete and simplified Y6.



Source: Author.

As can be seen from the CAFI result, the alkyl groups define inert regions of the molecule, as evidenced by their dark blue coloring. Note that the structures present very similar results. Therefore, it is safe to conclude that, in the context of this work, alkyl side chains are disposable.

About the CAFI itself, the major points of interest are the most reactive sites (orange to red atoms). These sites are: i) one of the N atoms of EGs, followed by ii) the core's central S atom (at the thiadiazole) and iii) the other N in the EG, in this order, for reaction towards nucleophilic agents (f^+). On the other hand, reactivity towards electrophilic agents (f^-) is present only in the central S atom. Finally, as f^0 represents the average between the other two indexes, it carries information from both, having as its main reactive site the central S and one of the EG's N atoms as the secondary site for reactions with free radicals. Note that Y6 reactivity presents a vertical symmetry, so that analyzing half of the molecule is enough to understand it as a whole.

A reaction with a nucleophilic agent means the system will lose a positive charge or gain a negative charge. In CAFI's calculation, this negative charge is exactly one electron. In short, f^+ indicates the sites where electrons are prone to enter the molecule. Consequently, f^- shows the sites where electrons are withdrawn. Notice that, although the thiadiazole's S can

do both actions, the EG's nitrogens are more likely to receive the electrons. Based on these results, the electron hopping processes in Y6 domains can occur in EG's N to thiadiazole's S. This hopping feature will be further discussed in CTFI analyses, once CAFI results are very limited in that regard.

The MEPs also show the vertical symmetry of Y6 (similarly to CAFI), indicating no dipole component in the horizontal direction. However, vertically it differs, indicating that Y6 holds a more pronounced negative charge on its bottom half. In fact, there is a dipole moment in this direction. The calculation displays a vertical dipole moment of 1.12 D, downwards (EG direction, higher negative net charge), for the simplified structure, and 1.52 D for the complete one, however, off-plane relative to the core (due to side chains), but also pointing towards EGs. Such dipoles have been reported and are regarded as a relevant feature for nonlinear optical properties of this material (ZHU et al., 2020). The presence of dipoles also indicates that negative charges can be drifted to the top half of Y6, towards the thiadiazole's S, that, in turn, are prone to interact with electrophilic agents. These features also indicate the ambivalent charge transfer characteristics of Y6 (ZHU et al., 2020).

Generally, CAFI showed Y6 as presenting a higher number of sites that are prone to interact with nucleophilic species, indicating its electron acceptor nature. Also, the core (everything but EG) defines an effective donor block of this NFA, hence the most reactive part for f^- . Lastly, the central part of the core is an electron-deficient ring, so it is not strange to see that it is also reactive toward nucleophiles (LU et al., 2021; YUAN; ZOU, 2022). The MEP evidences the Y6 dipole moment and shows that the EG's N and thiadiazole's S may attract positively charged particles through electrostatic effects.

In conclusion, it is possible to say that Y6 has preferred sites to receive and donate electrons (EG's N as acceptor and core's thiadiazole's S as a donor).

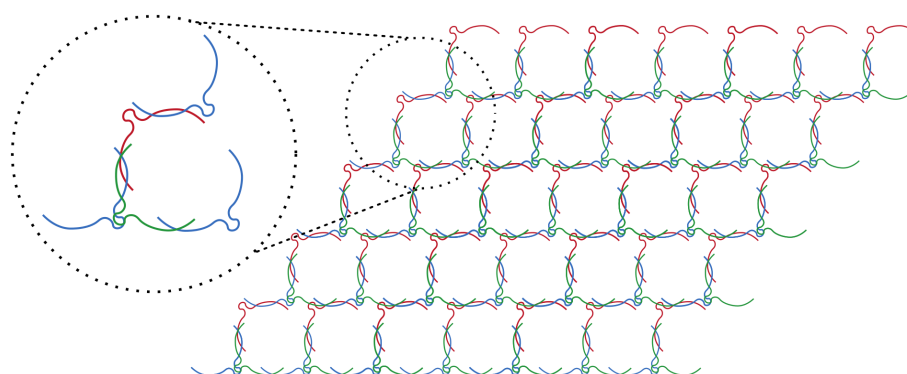
1.3.1.3. CTFI STUDY AND Y6 STACKING

A number of works indicates that Y6 has a triclinic crystalline structure, in which Y6 molecules interact via strong π - π stacking mainly involving the EGs, but also core/core and core/EG. The strong interactions result in a compact molecular packing measured by several experiments with intermolecular distances of around 3.5 Å. Different studies report that Y6 molecules build a plane-like 2D network for charge transport, and then many of these planes stack together to build a 3D interpenetrated framework of ambipolar charge transport (XIAO

et al., 2020; YAN et al., 2020; YUAN et al., 2019; ZHANG et al., 2020; ZHU et al., 2020a, 2020b).

The way this 3D network builds itself is fairly intricate. First, the most basic interactions need to be understood. Y6 molecules stack on each other through 3 main interactions, and due to their shape, building in interesting molecular dimers. The EG/EG stack constructs the so-called U and S-shaped Y6 dimers, while the core/core interactions build Y-shaped dimers (ZHANG et al., 2020). There are reports of a fourth interaction, also an S-shaped dimer, but instead of EG/EG, it's an EG/core interaction (ZHU et al., 2020a, 2020b). To illustrate this, Figure 1.7 shows a simplified version of these four interactions and how they build into a 2D network. Three different colors were used to represent the different planes.

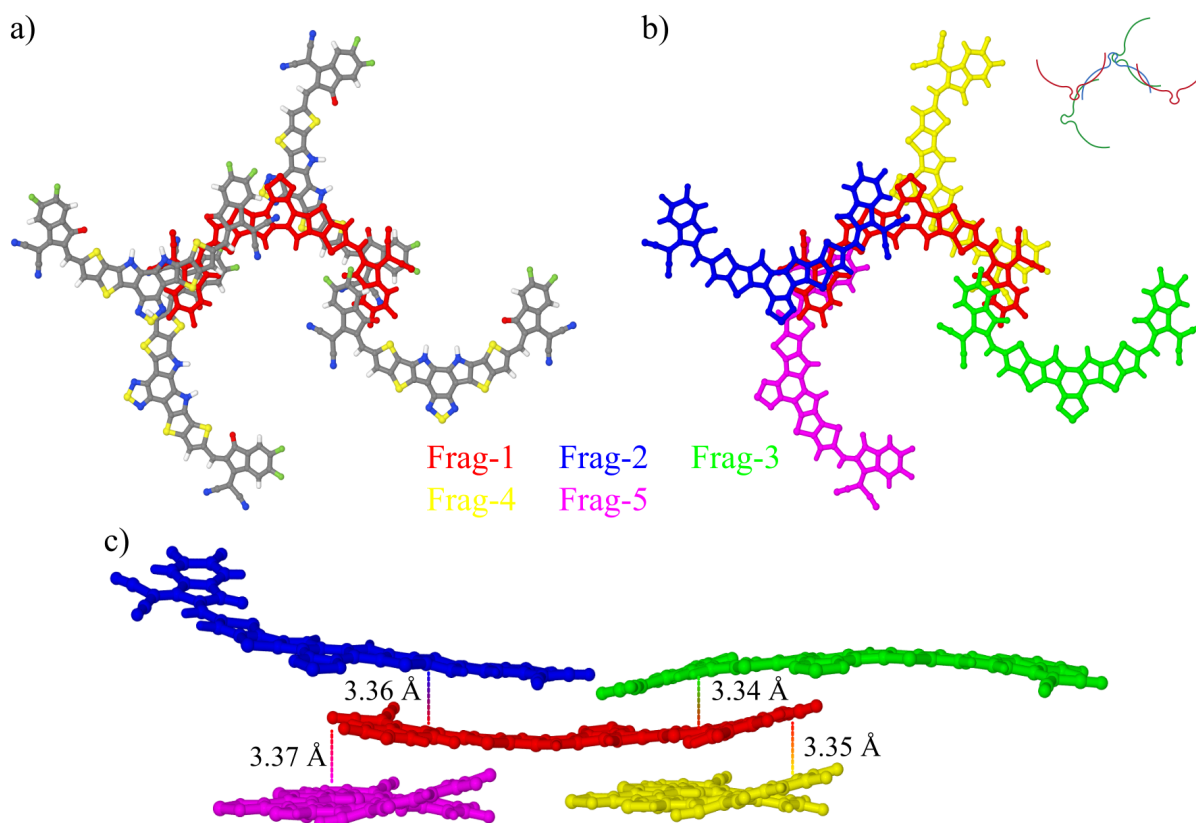
Figure 1.7. Scheme of a simplified 2D network of Y6s



Source: Author.

To understand the charge transfer process in this intricate network, CTFI defines an interesting tool, as it's able to evaluate each kind of molecular dimer interaction reported in many studies. The study of Weigang Zhu *et al.* named "Crystallography, Morphology, Electronic Structure, and Transport in Non-Fullerene/Non-Indacenodithienothiophene Polymer:Y6 Solar Cells" provides as a Supplementary Material, both the CIF file (data for periodic crystallographic calculations) and the XYZ file for five fragments that builds the four different interactions (ZHU et al., 2020b). Figure 1.8 shows the different interactions to be studied by CTFI.

Figure 1.8. Y6s' molecular dimer interactions used for the CTFI study: a) the structure itself with the main fragment highlighted, also in b) each fragment highlighted in different color for clearer view, with simplified version in the top rightmost corner, and c) these fragment π - π interaction distance.



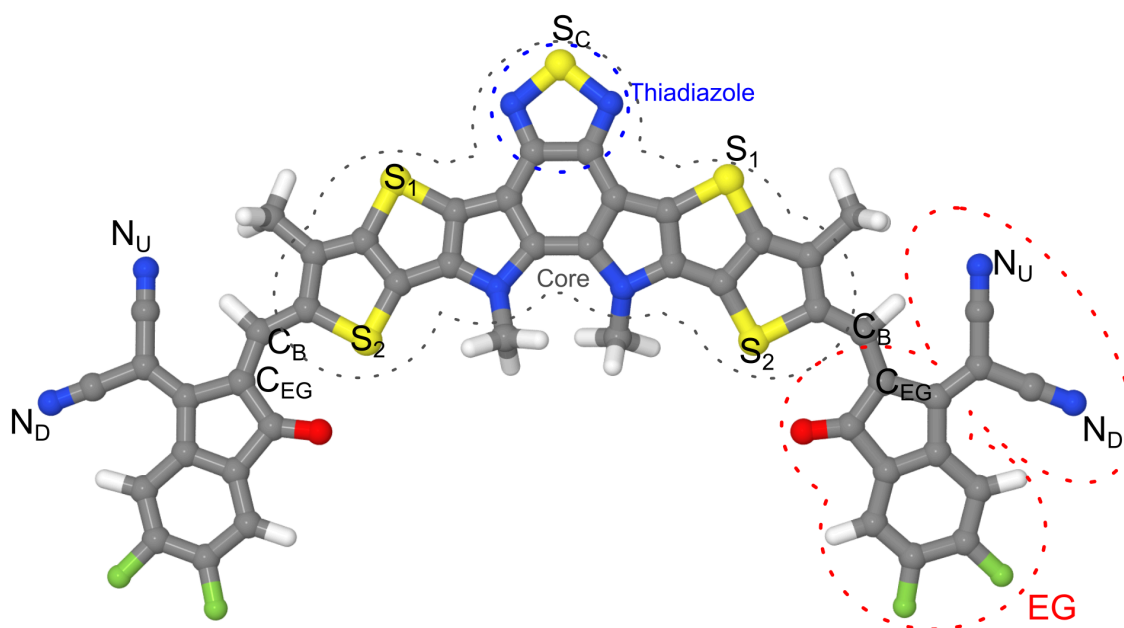
Source: Author.

Notice that Frag1 has been highlighted in (a) to make it clear that it is the one molecule that interacts with every other one (strong π - π). In the plane above Frag-1, it interacts with Frag-2, building dimer-S1, and with Frag-3, building dimer-S2. On the other hand, in the plane below, Frag-1 interacts with Frag-4 and Frag-5, and builds the dimers Y and U, respectively. It is also important to note that these structures are different from the ones in CAFI's results (they use only an H atom in place of the alkyl chain), and they are slightly different among themselves. Each molecular dimer also presents a slightly different π - π interaction distance, seen in c).

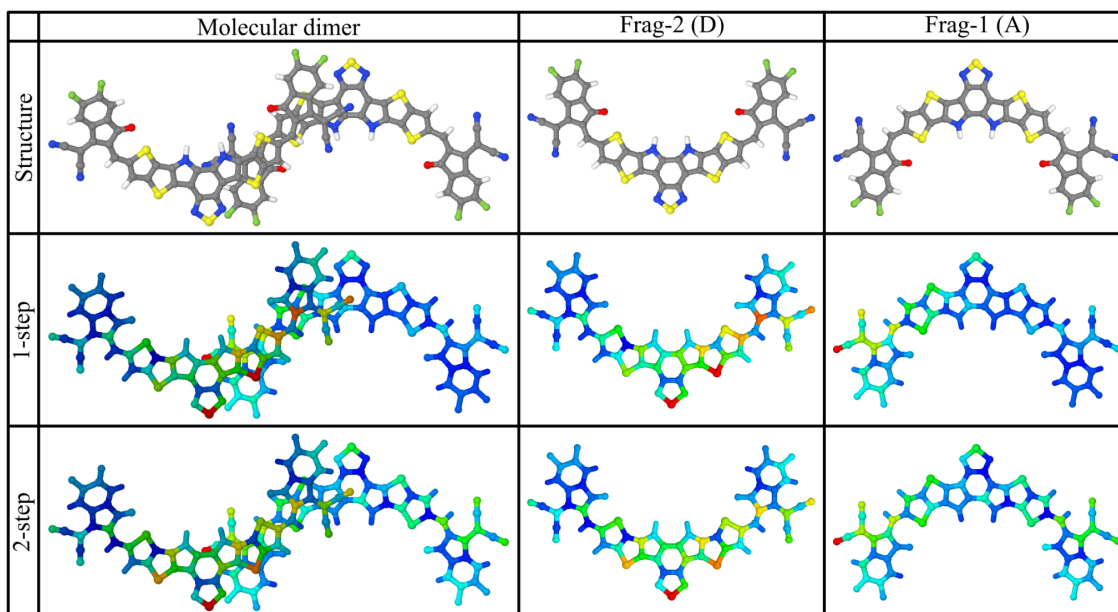
Each molecular dimer mentioned above was built with the data from Weigang Zhu's work and their CTFI (1- and 2-step) was calculated. Remember that CTFI calculations separate the molecular dimer into A and B, acceptor and donor of subunits, respectively. Which is a no problem for these dimers, since they are made with two of the same molecules,

being a somewhat symmetrical dimer where A and B definition is not important. Figure 9 brings a Y6 structure with highlighted features to assist the CTFI discussion, while Figures 1.10 to 1.13 represent these results for aforementioned combinations, dimers S1, S2, Y and U, respectively, where Frag-1 is always set as A. The color follows the same RGB scale as CAFI results. However, molecules other than Frag-1 are colored in a darker shade.

Figure 1.9. Y6 with important atom and region naming.



Source: Author.

Figure 1.10. Y6s' S1 molecular dimer CTFI results.

Source: Author.

For S1 dimer it is noticed a situation where there is EG/core interaction. Note that, for both 1- and 2-step, as Frag-2 assumes the “B” role (donor part of the system), its core presents more highly reactive sites (red/orange) than its EG. Conversely, Frag-1 (“A” molecule) has N_D as the most reactive atom, highlighting its acceptor capability. Another generic behavior is the non-symmetrical spatial distribution of the reactivity, since they are now interacting with each other, the once observed symmetry is lost.

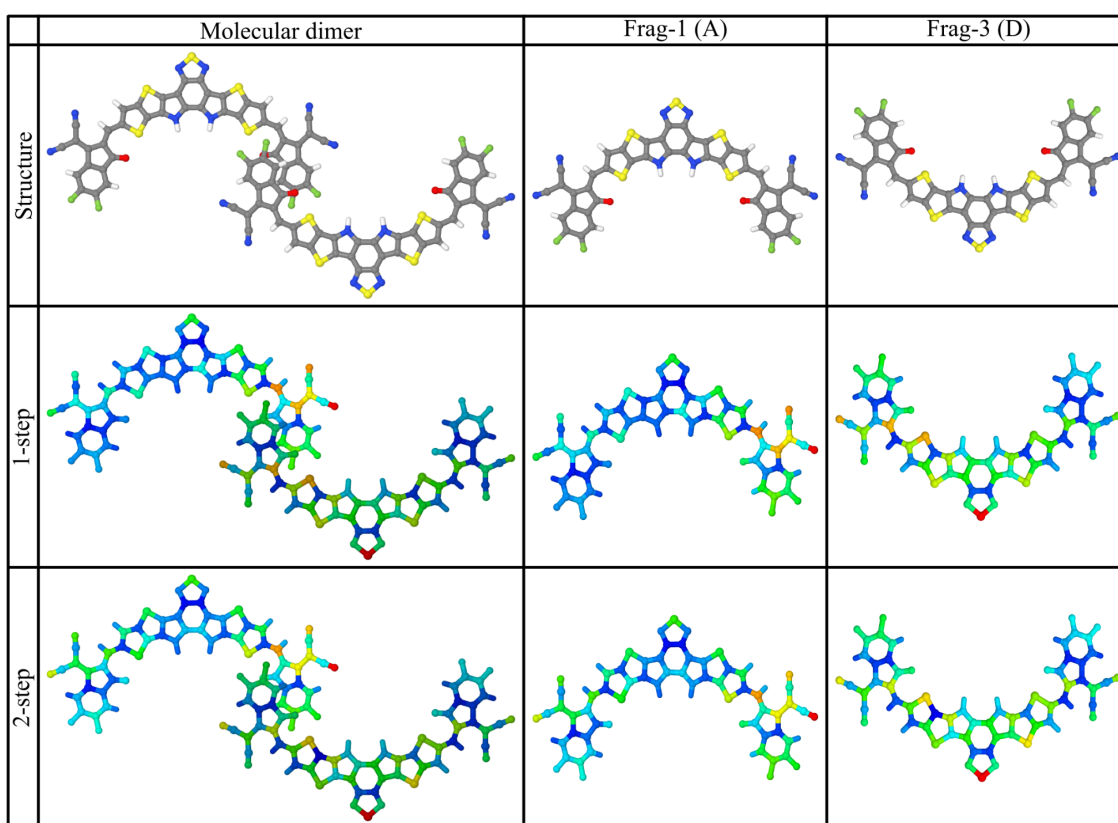
Comparatively, 2-step CTFI results seem to be slightly less reactive than the 1-step counterpart. That means that, in general, the most reactive sites are preserved, but they present reduced reactivity. Independently of this difference, both methods show the same qualitative result.

When comparing Y6's CAFI results it some novelty is noticed. In this configuration, the electron accepting route seems to be centered on N_D , which was also a very reactive f^+ site, but for CAFI, the N_U and S_C were also important sites (though less reactive). On the other hand, the electron-withdrawing sites increased in the CTFI results, besides the highly reactive S_C , other core's atoms and even some of EG's atoms presented enhanced reactivity.

In general, it is noticeable that the Y6 core is the most important part when the molecule is acting as a donor, while EG dominates the electron acceptance processes. These statements are in accordance with the A-DA'D-A definition of the Y6 and the CAFI results (SHOAEE et al., 2023; YUAN; ZOU, 2022). However, with CTFI results, it is possible to

trace a better route for the charge carriers. In the S1 dimer, electrons have multiple releasing routes, however, as there is only one acceptor site, the most likely donor center is the one closest to the entrance. In this context, electrons in Y6 might be released from S_c and S_1 atoms to enter the other Y6 by N_D .

Figure 1.11. Y6s' S2 molecular dimer CTFI results.



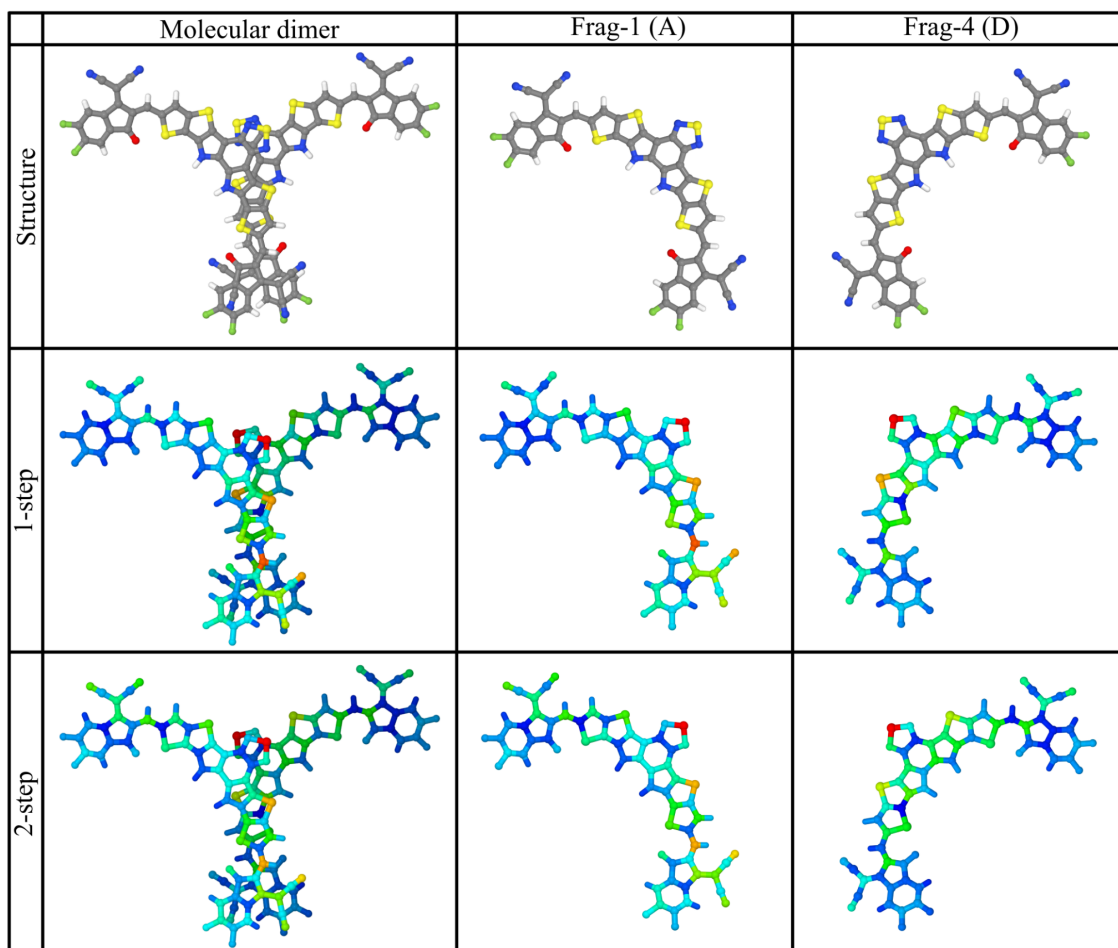
Source: Author.

Some of the previously discussed observations for S1 results reappear for S2. It is again noticed that the asymmetry in CTFI sites, with the 1-step approach being slightly more reactive than the 2-step (presenting the same reactive sites). Frag-1 ("A" role) presents a more reactive EG region while Frag-3 ("B" role) has a more reactive core. These are the similarities with S1. However, for the S2 dimer, the interaction takes place between two EG units, which leads to some differences.

Compared to dimer-S1, S2's core is less reactive for B due to the lack of EG/core interactions. On the other hand, the reactive part of Frag-3's EG group (especially visible in 1-step) is far more important now. The electron route for this dimer involves two interacting

EGs, so it is supposed that electrons leave Y6 from the N_D or C_{EG} , going to C_B (and maybe N_D/N_U).

Figure 1.12. Y6s' Y molecular dimer CTFI results.



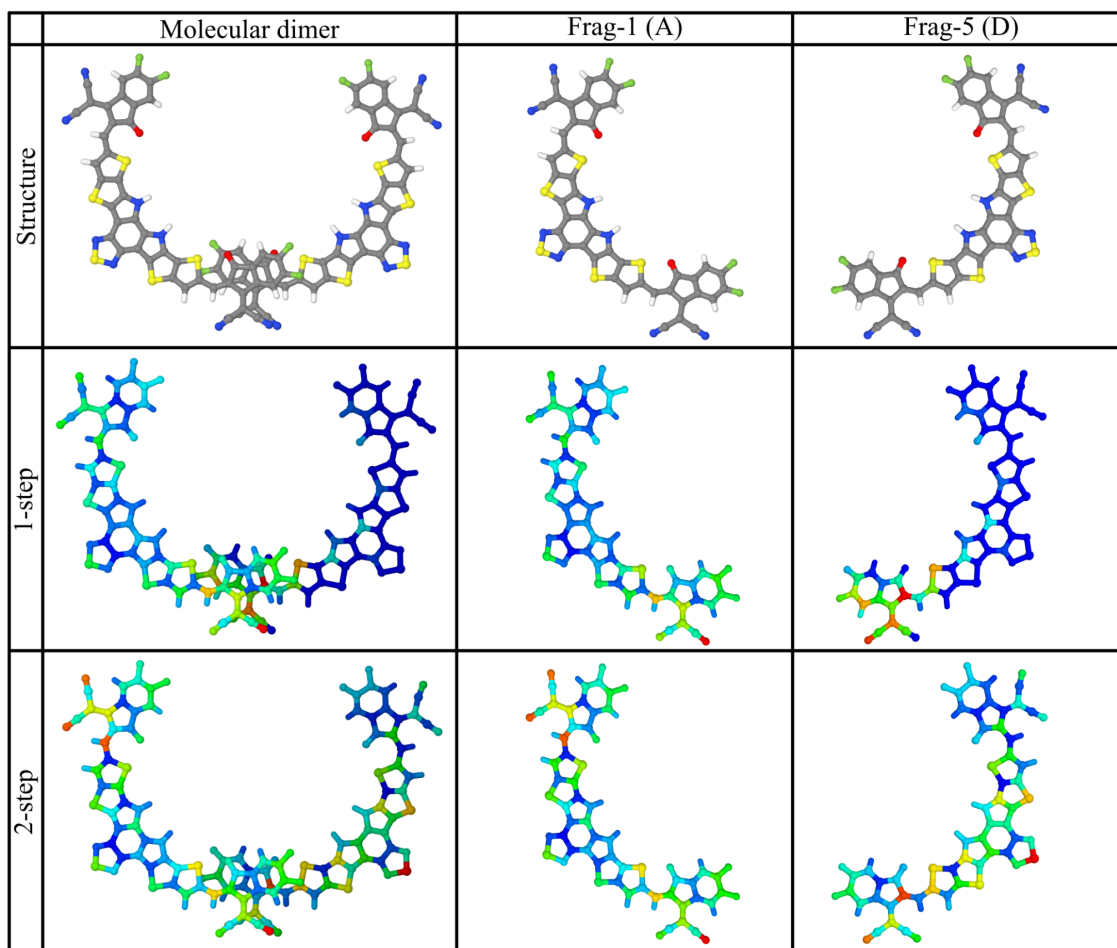
Source: Author.

Dimer-Y offers a very distinct core/core:EG/EG interactions. For the S2 dimer, the EG/EG interaction led to the donor's EG being more important than usual. Here, it is noticed a greater than usual (for CTFI) importance of the acceptor's core. Despite the differences, the previously mentioned generic characteristics still appear.

Here, as the third dimer to be studied, some patterns started to emerge. The acceptor generally has a reactive site in N_D and/or N_U (S1, S2, and Y) and the C_B (S2 and Y). The acceptor unit usually shows as reactive sites the S_C , S_1 (S1, S2, and Y), and C_{EG} (S1 and S2). These mentioned patterns, even when not appearing as highly reactive (red/orange) they still appear as more reactive than their surroundings.

Finally, the electron route in dimer-Y can be pinpointed to the core, at S_C , which is supposed to donate and receive electrons from one side to the other. This result is similar to the one obtained from CAFI calculations.

Figure 1.13. Y6s' U molecular dimer CTFI results.



Source: Author.

For this last dimer, there were some unexpected negative values, hence the amount of dark blue sites. This and previous calculations gave no negative values for the A unit. Conversely, for the B unit, previous calculations led to no negative values in 1-step CTFI and occasional 1 negative value in the 10^{-3} order for the 2-step, which in absolute values is small compared to the positive results. For the U dimer, however, the 1-step approach leads to quite a few 10^{-3} order negatives, more than desirable, but not the worst. The 2-step calculations were also fine, without any significant negative value.

Dimer-U brings another EG/EG interaction, similar to S2. Due to negative values, Frag-5 EG's sites look more reactive than they probably really are, due to how colors are selected from normalization. Either way, the expected can still be seen, both A and B having their EG region more reactive than the rest. Despite the negative value problems, the previously mentioned general behavior and observed patterns can be noticed once again, and therefore confirmed as a generic feature.

In relation to the electron transfer route, it should be most likely happening through N_D on both ends of the transference.

In conclusion, several patterns and generic behaviors can be noticed from Y6's dimer CTFI results. First, there are preferences for highly reactive sites. "A" molecules tend to present more reactive EG, while "B" molecules present a more reactive core, it all depends on which regions they are interacting (EG/EG, core/core, or EG/core). Furthermore, the reactive areas tend to activate specific atoms for "A" or "B" molecules. For instance, the "A" ones tend to have a reactive C_B atom. Conversely, in "B" molecules, the C_{EG} is the one reactive. Also, the not-surprising asymmetry in site distribution is easily noticeable. Moreover, these calculations allowed for mapping charge carrier routes, which combined with its crystalline structure easily show the reported 2D and 3D ambipolar charge transfer network (ZHANG et al., 2020; ZHU et al., 2020a, 2020b).

Finally, CTFI demonstrates a strong correlation with CAFI, in the most reactive sites and preferred reactive regions, considering donor or acceptor behavior. It's possible to rationalize both results together: CTFI considers CAFI but enhances the reactivity in the interacting regions. The CTFI proves to be a valuable tool for identifying and proposing charge transfer pathways, being a complementary tool to use alongside CAFI and MEP.

Besides these results, the dipole moment was also calculated for each pair. Their values are varied and higher than individual Y6, with the exception of dimer-S2. Table 1.2. show these mentioned results.

Table 1.2. Dipole moment results, in Debye (D), for Y6s and their dimers.

Structure	Dipole moment intensity (D)
Dimer-S1	3.548
Dimer-S2	0.267
Dimer-U	2.586

Dimer-Y	3.333
Y6 (CH ₃ substituted)	1.123
Y6	1.520

Source: Author.

Remember that in the dimers, all the alkyl chains were changed to H by Weigang Zhu and collaborators, while this work's simplified Y6 has CH₃ for substitution. Anyway, it was seen a major tendency for an increase in the dipole moment, which in the repeating cell results in the 2.17 D moment calculated by Zhu *et al.* (ZHU et al., 2020b). The direction of the molecular dipoles in the dimers was always pointing from Frag-X to Frag-1 (X=2, 3, 4 or 5), whilst the stacking cell dipole was depicted as following Frag-3 curvature and plane (ZHU et al., 2020b). The dipole moment direction shows the direction in which positive charges are prone to go (due to the electric field from the molecular dipole itself). In the case of molecular dimers, it shows a tendency of the electrons being released from Frag-1 to the environment. In the grand scheme, however, the whole unit cell molecular dipole indicates a more general direction (to where Frag-3's thiadiazole is pointing) that would be in the thin film. Remember that Y6 (and Y6:PM6) thin films are parallel to the substrate/electrodes, therefore, the discussed molecular dipole should not affect the charge transport towards the electrodes (ZHANG et al., 2020; ZHU et al., 2020a, 2020b).

For the sake of completeness, CAFI was calculated for all four dimers. Its interpretation should be the same as always, which means the results will show how external agents interact with a dimeric system of Y6s. The results bring nothing new and reinforce the necessity of CTFI as an approach to studying dimeric systems. For the above reasons, these results are presented separately in Appendix I.

1.3.2. D18 STUDIES

As mentioned, the NFA:Polymer combinations of Y6:D18 and Y6:PM6 are the focus of this work as they are in the vanguard of highly efficient OSC (LIU et al., 2020; WEI et al., 2020). In the following subsections, isolated D18's structural and properties studies are displayed.

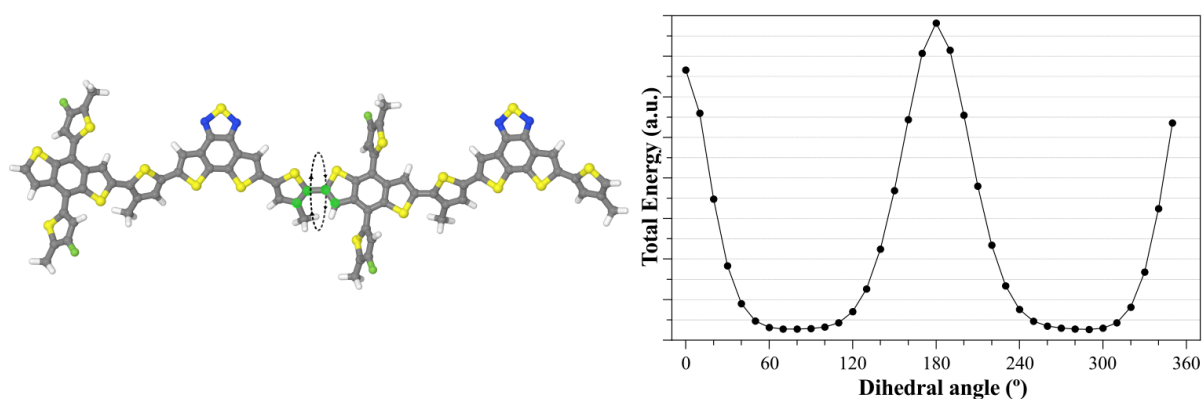
1.3.2.1. STRUCTURAL AND SATURATION STUDIES

For polymeric structures it is necessary to start with the regular structural study of the molecule, in this case the monomer, as done for Y6. This process is similar to every molecule, KingDraw and Avogadro softwares were used to build the 2D stick structure and convert it to 3D one, respectively (HANWELL et al., 2012; KINGDRAW, 2019). Also, as seen for Y6, alkyl side chains were substituted by a methyl molecule, which significantly reduces the degrees of freedom (and computational cost, consequently) without jeopardizing the properties calculations.

The process described in Section 1.2.2.1. were followed to successfully build a D18 monomer, which can then be used to conduct the saturation process (explained in Section 1.2.2.2.). Before starting the saturation itself it is necessary to evaluate the dihedral angle between two monomers, and then define which ones to use. It is important to highlight that D18 thin films show strong π - π interactions, which requires quite planar structures (XIAO et al., 2020). Therefore, angles much different from 0° or 180° are not likely to appear after optimization.

One D18 dimer was then built and submitted to a dihedral angle scan. In this process the dihedral angle between the monomers were selected and set to change 10° at each step for 36 steps. For each step a single point calculation was made to estimate the dimer's total energy. Figure 1.14 shows how the scan was made and the obtained results.

Figure 1.14. D18 dihedral scan study; green highlighted atoms indicate the atoms composing the scanned dihedral angle. 0° corresponds to configurations with carbon atoms of thiophene rings on the same side.



Source: Author.

The results indicated that 80° and 290° (-70°) are good starting dihedral angles for optimization. Therefore, to investigate beyond the scan, four 2 unit D18 (here called D18-2mer) with different initial dihedral angles were fully optimized to find the lowest energy conformation's dihedral angles. The angles were 80° and 290° , from scan result, and 0° and 180° , an initial planar configuration. Table 1.3 shows these results.

Table 1.3. Initial and final dihedral angles and total energy (eV) of optimized D18-2mer structures.

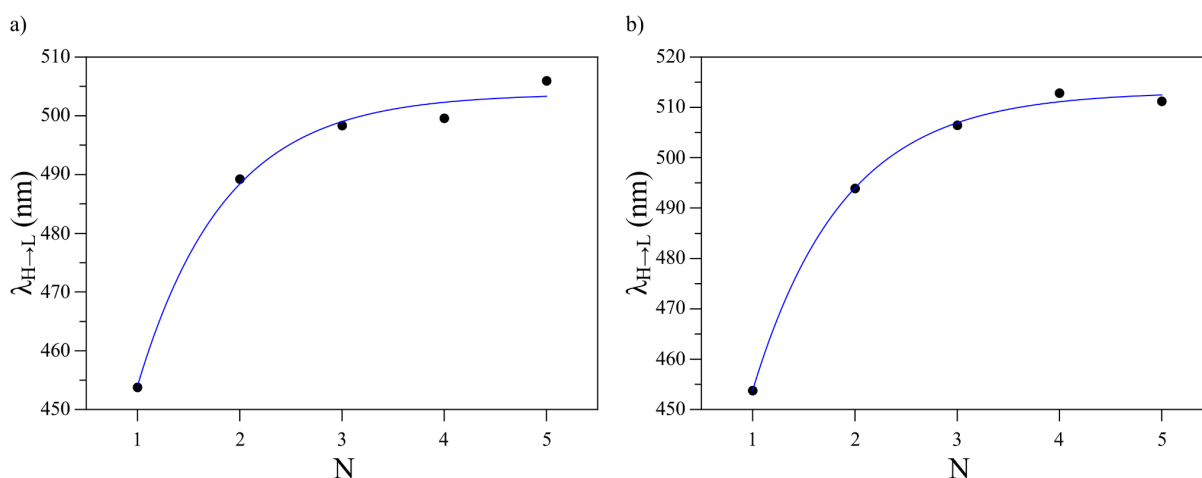
Initial dihedral	Final dihedral	Total energy (eV)
0°	-30°	-295506.06
80°	30°	-295506.06
180°	157°	-295506.06
290°	$330^\circ(-30^\circ)$	-295506.06

Source: Author.

First, notice how the energy is the same for all structures, indicating they are equally probable to happen. This study points to basically 4 different possible angles: 30° , -30° , 160° and -160° . The $30^\circ/-30^\circ$ pair build the straightforward structure, while the $160^\circ/-160^\circ$ builds an alternating structure. Also, for the sake of simplicity, these different pairs will not be mixed in the same structure. However, the pair alternates, *i.e.* 30° , -30° , 30° and so on, otherwise the structure will spiralize while growing.

With dihedrals calculated, Meier's approach for polymer saturation was applied (see Section 1.2.2.2.). The molecules are named D18-*n*mer and D18-*n*mer-alt, for the straightforward ($30^\circ/-30^\circ$) and alternating structures ($160^\circ/-160^\circ$), respectively, with *n* indicating the number of repeating units. Figure 1.15 shows the Meier's approach results as graphs of first transition peak transition ($\lambda_{H \rightarrow L}$) in nanometers (nm) versus the number of repeating units (N), for both types of structure. Table 1.4 shows the data from Meier's equation (Equation (1)).

Figure 1.15. D18 Meier's fit result for structures with (a) straightforward and (b) alternating structures.



Source: Author.

Table 1.4. Meier's equation data on D18 saturation.

	straightforward	alternating
a	1.132	1.175
$\Delta\lambda$ (nm)	59.34	49.82
λ_{∞} (nm)	513.10	503.76
n_{ef}	4.3	4.6

Source: Author.

As it can be seen by the graphs, the maximum size made was D18-5mer structures. Meier's approach requires unfeasible calculations for bigger structures. However, it was not a problem, as Table 1.4 shows that D18 oligomers with four to five repeating units can already be considered as saturated.

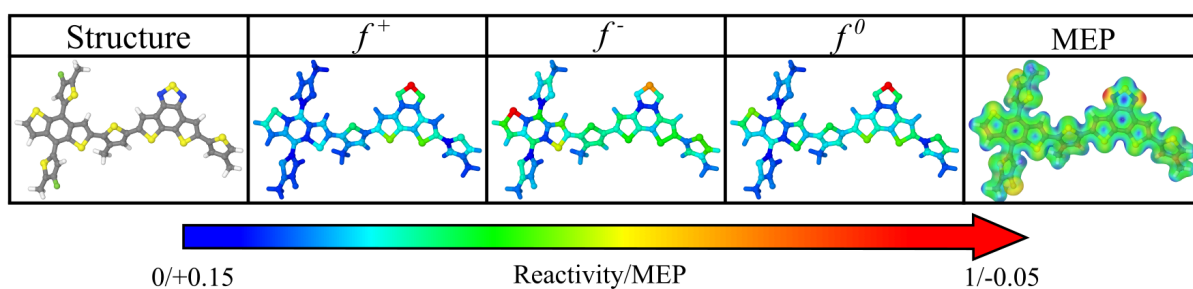
In conclusion, D18 shows itself as a somewhat planar molecule ($\sim 20^\circ$ to 30° off plane) with a rather complex structure that makes more complex calculations for structures larger than five units. However, results from Meyer's fit method show saturation effects around four units. Other traditional semiconducting polymeric systems commonly present bigger n_{ef} values, such as 17 for MDMO-PPV or 15 for polypyrrole derivatives (COLEONE; LASCANE; BATAGIN-NETO, 2019; GALINDO et al., 2023). This feature is related to the monomer's A-D composition, which restrains the conjugation to fewer units.

One last note about D18's structure is that its straightforward configuration starts to bend in a C-like shape in relation to its longitudinal axis, very evident in D18-5mer. This, however, comes from entropy "forces" which act in the sense of increasing the system's disorder (by curving it). The entropy force appears because when polymers grow in size (in the plane) it gets increasingly organized, which goes against the laws of thermodynamics (CALLEN, 1985).

1.3.2.2. CAFI AND MEP RESULTS

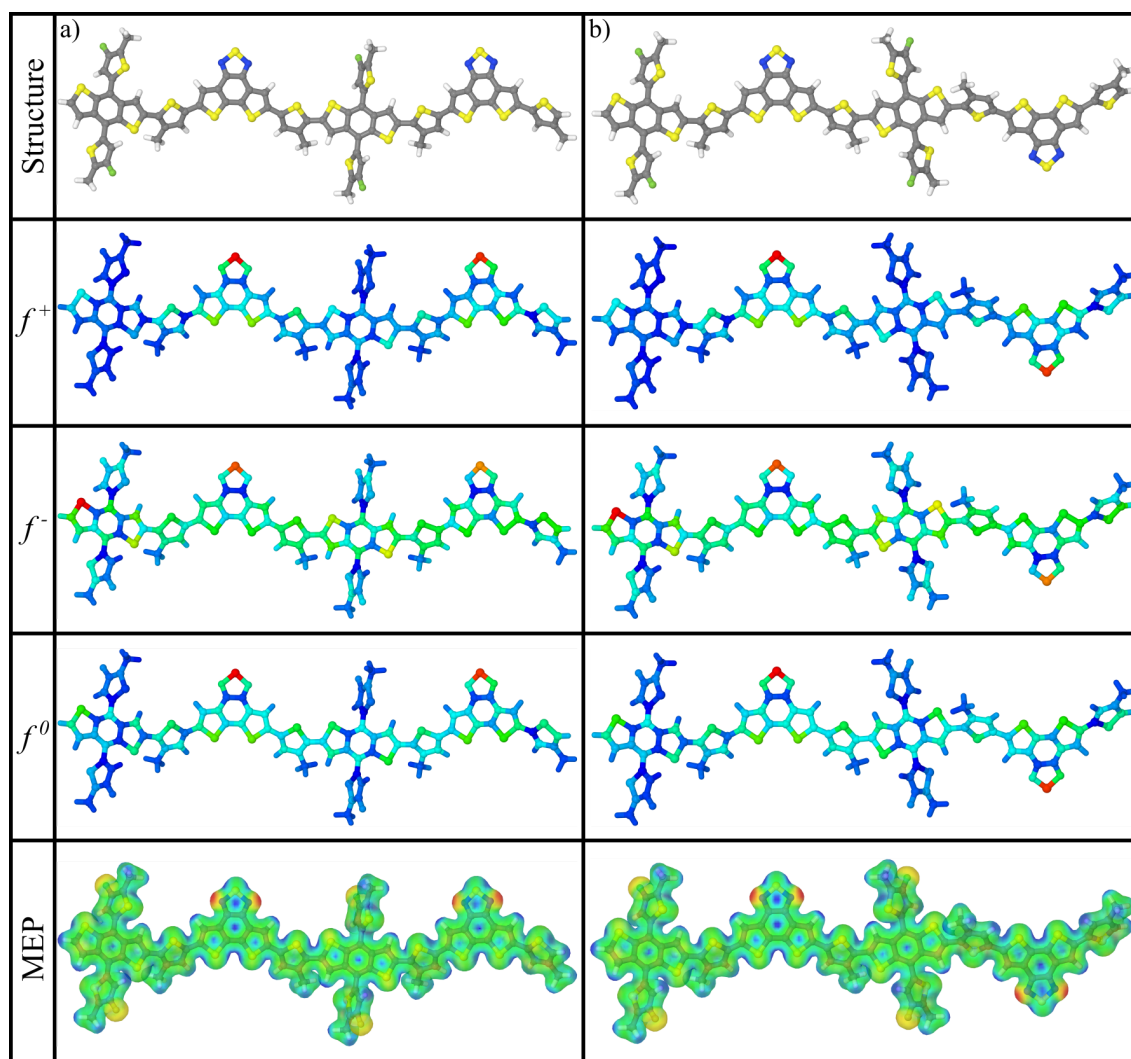
As stated in the previous section, CAFI and MEP calculations for D18 were made for five different sizes (D18-1mer to D18-5mer), for the two types of structure. Figures 1.16 to 1.21 show these results. The first of these figures also brings the RGB scale used for both reactivity and MEP.

Figure 1.16. CAFI and MEP results for D18-1mer.



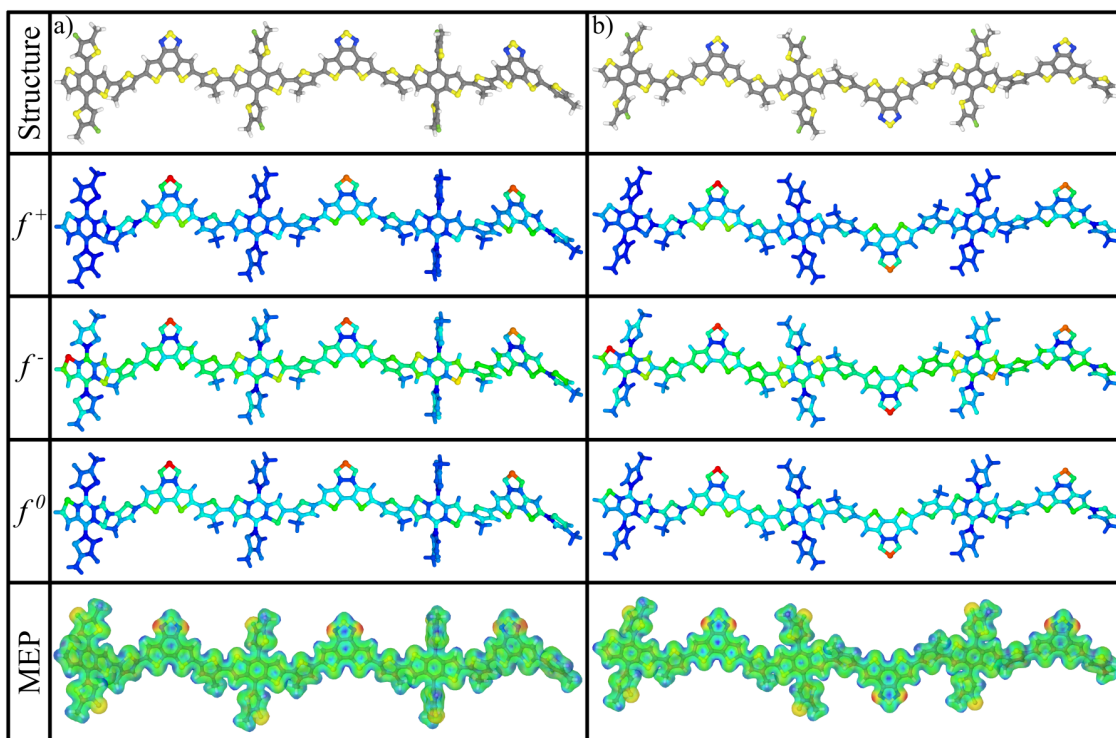
Source: Author.

Figure 1.17. CAFI and MEP results for D18-2mer, a) straightforward and b) alternating.



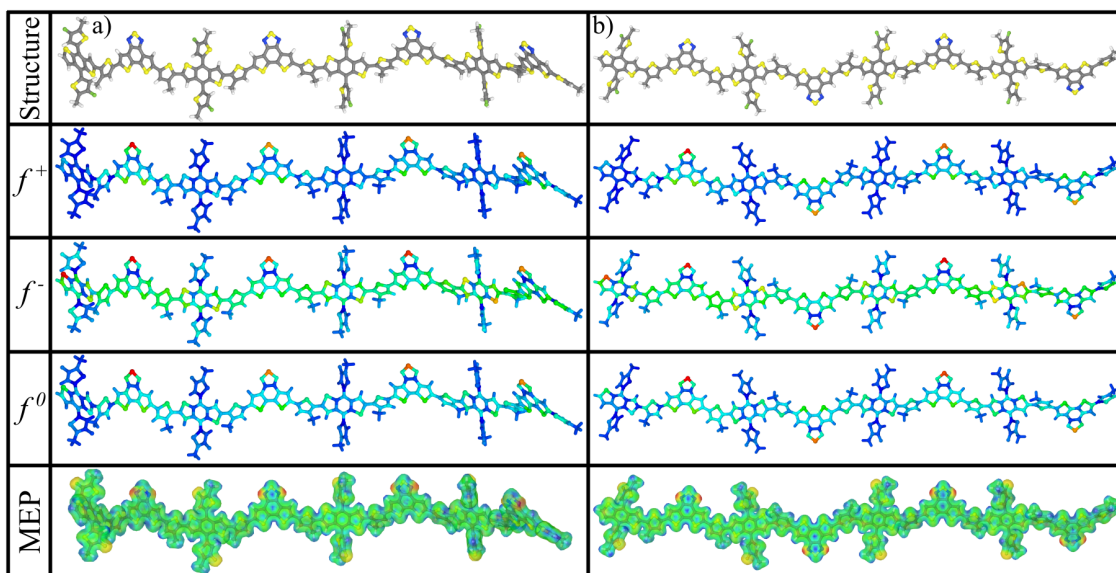
Source: Author.

Figure 1.18. CAFI and MEP results for D18-3mer, a) straightforward and b) alternating.

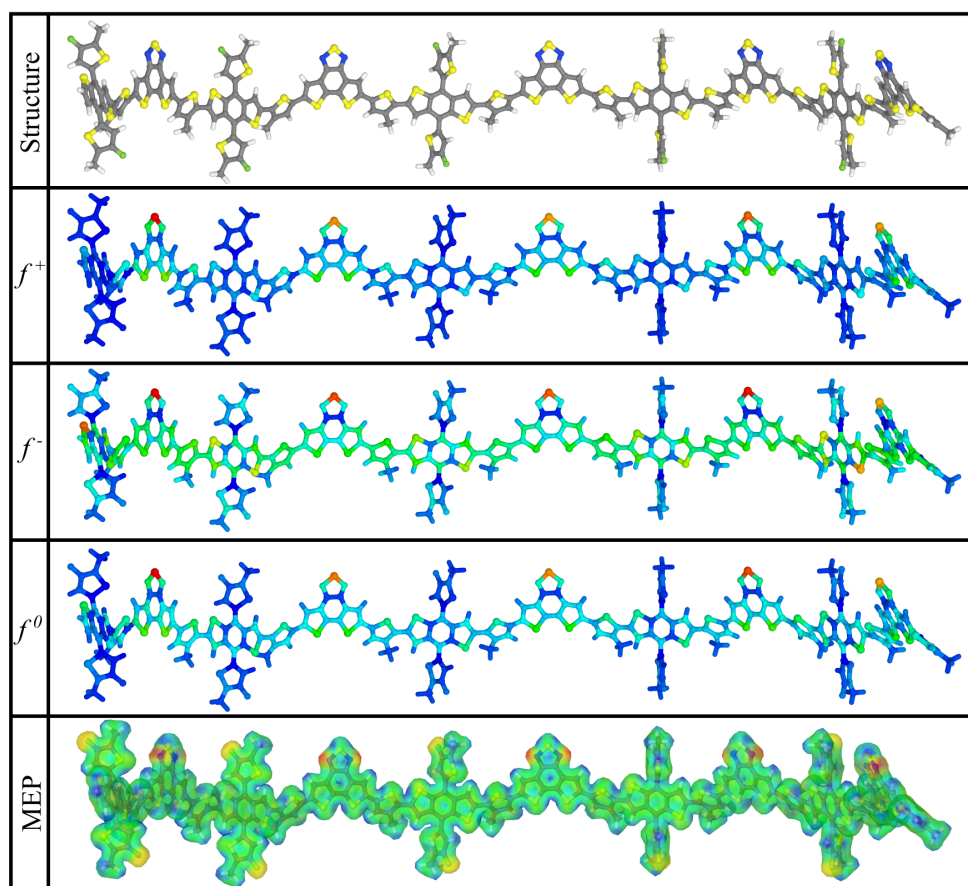


Source: Author.

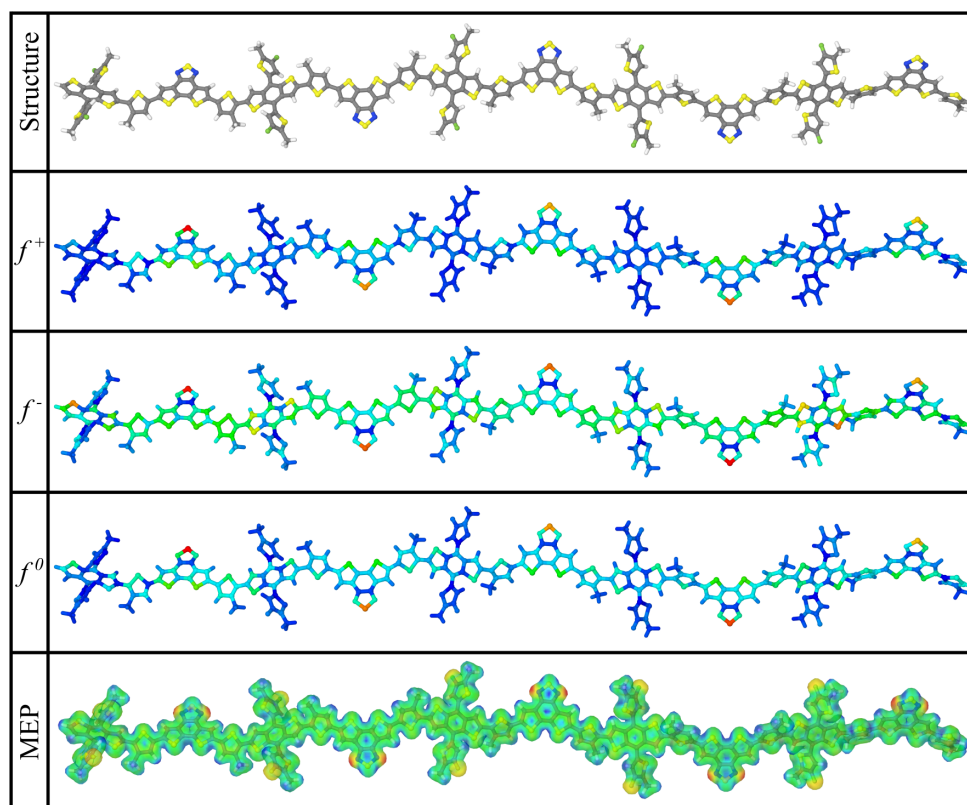
Figure 1.19. CAFI and MEP results for D18-4mer, a) straightforward and b) alternating.



Source: Author.

Figure 1.20. CAFI and MEP results for D18-5mer.

Source: Author.

Figure 1.21. CFI and MEP results for alternating D18-5mero.

Source: Author.

Note that thiadiazole's S atom is the most reactive site in relation to f^+ of D18-1mer, indicating that it is prone to accept electrons. The rest of the molecule, however, has a very poor reactivity. Conversely, f^- shows this same site as the most reactive towards electrophilic agents, as well as an even more reactive site in the leftmost S atom. These are the sites prone to donate electrons, the overall reactivity in the molecule is low, however higher than for f^+ . These results evidence the predominant donor nature of D18, however, also show some electron acceptance capability.

The MEP shows an overall neutral molecule with distinct negative charges on N atoms, and positive charges on Fluorine. The positive charge regions could have an impact on attracting electron-rich regions of adjacent molecules, allowing the electron capture via S atom. This behaviour might support an ambivalent charge transport on D18, similar to what is observed for Y6 (ZHU et al., 2020b).

Figures 1.17 to 1.21 show that the main features of D18-1mer can be also noticed in more extended structures. It is noticeable that the middle section of the D18 oligomer is quite uniform, in the sense that the repeating units show the same reactive patterns: a highly

reactive S atom for thiadiazole. On the other hand, the leftmost and rightmost units show some different reactive sites (f^-), similar to the monomer's f^- sites. It is important to note that although the mean reactivity for f^+ is not as high as f^- , highly reactive sites are still present in the whole polymer, showing its electron acceptance ability. Lastly, there were no signs of reactivity difference between alternating or straightforward structures.

There are no MEP differences between D18-1mer to D18-5mer, the same behavior is repeated throughout the units. This however shows a possible stacking configuration of these systems. It is well known that D18 has π - π face on stacking and is highly crystalline (ZHU et al., 2022), however MEP shows that, if perfectly aligned, some repulsion should appear, especially regarding the N atoms. Therefore, in a D18:D18 stacked structure, one of the units must be slightly shifted vertically, or a greater shift sideways. Another possibility is to have alternating units that help mitigate this repulsion effect.

In conclusion, D18 showed a clear donor character, given its high f^- reactivity, however, it also showed good electron acceptance capability (f^+ and MEP results). Therefore, D18 appears to have a similar ambivalent charge transport character like Y6. Moreover, MEP gives some information regarding how D18 stacks.

1.3.3. PM6 STUDIES

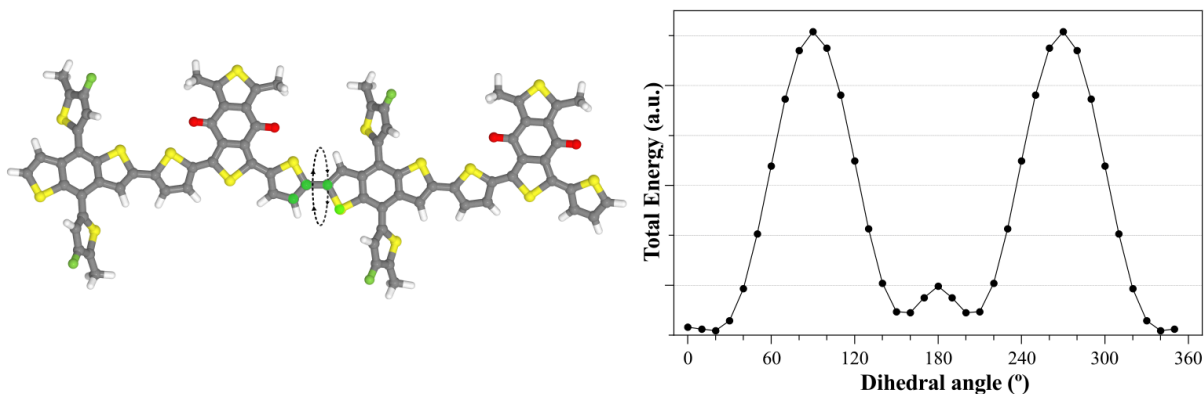
One of the NFA:Polymer combinations that is the focus of this work is Y6:PM6, once it defines one of the combinations in the vanguard of highly efficient OSC (LIU et al., 2020; WEI et al., 2020). In the following subsections isolated PM6's structural and properties studies are presented and discussed.

1.3.3.1. STRUCTURAL AND SATURATION STUDIES

For PM6, this step is pretty much the same as D18's, given both are polymers and are also quite similar in relation to their structures. PM6 is actually a precursor of D18 in the realm of donor polymers applied to OSC (WEI et al., 2020).

Recalling the process applied to D18, there is the general monomer building process, then the search for an optimal dihedral angle between two units, and finally growing the polymer and studying its saturation. The same monomer building process and procedure done for D18 was employed. The dihedral angle study was made in the same fashion as discussed in Section 1.3.2.1. Figure 1.22 shows these results.

Figure 1.22. PM6 dihedral scan study; green highlighted atoms indicate the atoms composing the scanned dihedral angle. 0° indicates conformations in which S atoms of terminal thiophenes are placed at opposite sides.

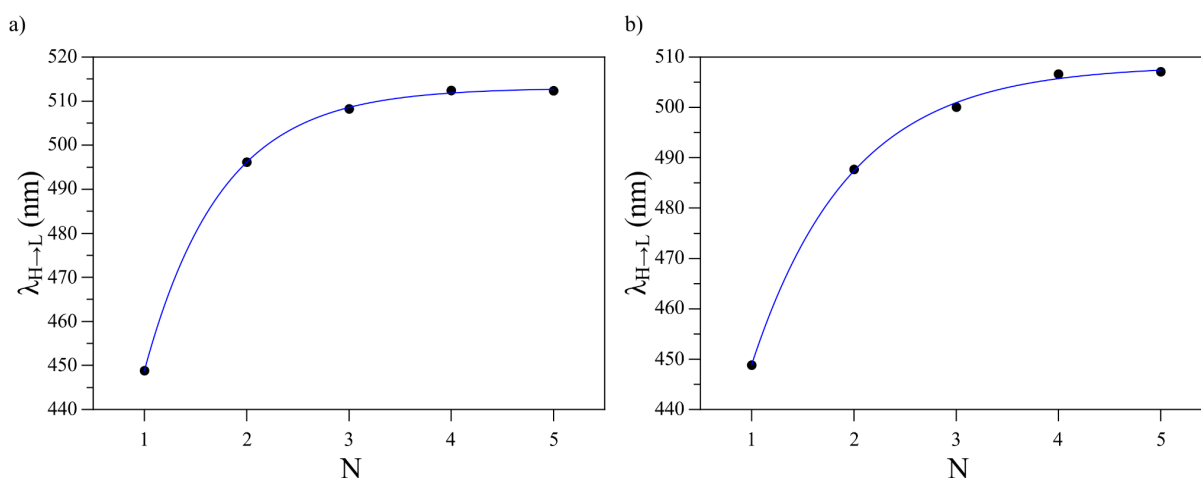


Source: Author.

Notice that the overall behavior observed for PM6 is very different from D18's one. Here the initial best angles are around 20° and 160° or 200°, for alternating structures. From these initial guesses we've obtained the final best dihedral angles to be used: $\sim\pm 10^\circ$ and $\sim\pm 160^\circ$, for straightforward and alternating structures, respectively. Also in the same fashion of D18's discussion, these values are used to build the input for optimization, where they are allowed to change and find a better conformation.

Sequentially, Meier's saturation approach was applied. Figure 1.23 shows the Meier's approach results as graphs of the first transition peak transition ($\lambda_{H\rightarrow L}$) in nanometers (nm) versus the number of repeating units (N), for both types of structure. Table 1.5 shows the data from Meier's equation obtained from the equation fitting process.

Figure 1.23. PM6 Meier's fit result for structures with (a) straightforward and (b) alternating structures.



Source: Author.

Table 1.5. Meier's equation data on PM6 saturation.

	straightforward	alternating
a	1.336	1.044
dλ (nm)	64.18	59.45
λ_∞ (nm)	513.00	508.30
n_{ef}	4.1	4.9

Source: Author.

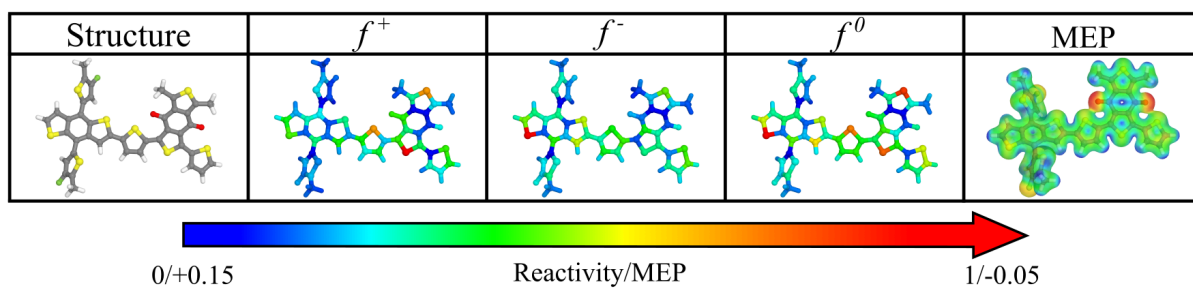
One can see that saturation is achieved around four repeating units for straightforward, or closer to five for alternating structures. The result is similar to the previous D18's ones. This isn't anything unexpected since both donor polymers are quite similar in structure (and π system). Similarly to D18, PM6-5mer achieved saturation at the computational limit, as a 6-mer unit was impossible to optimize with M06HF. However, DFT/B3LYP/6-31G(d,p) was possible for PM6-6mer, therefore, CAFE and MEP could be done (though not relevant). What is more evident for PM6 saturation is that alternating structures lead to slightly higher n_{ef} .

Regarding the structure, the bending noticed for D18 is also present in PM6, however, not as intense as previously noticed.

1.3.3.2. CAFI AND MEP RESULTS

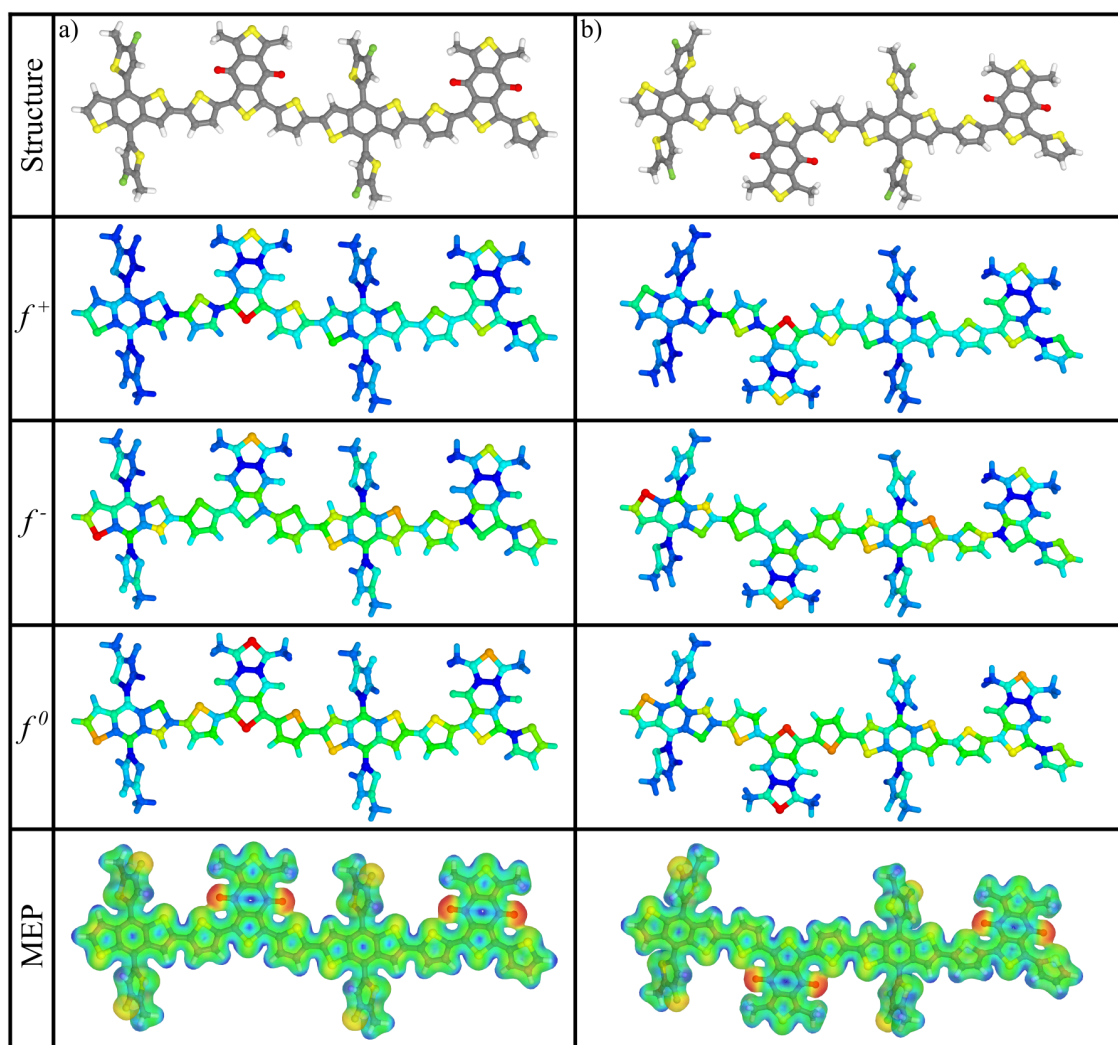
Figures 1.24 to 1.29 show the CAFI and MEP results of PM6 estimated for oligomers from one to five repeating units. The RGB scale used for both reactivity and MEP is the same as the one for D18 (also shown in Figure 1.24).

Figure 1.24. CAFI and MEP results for PM6-1mer.



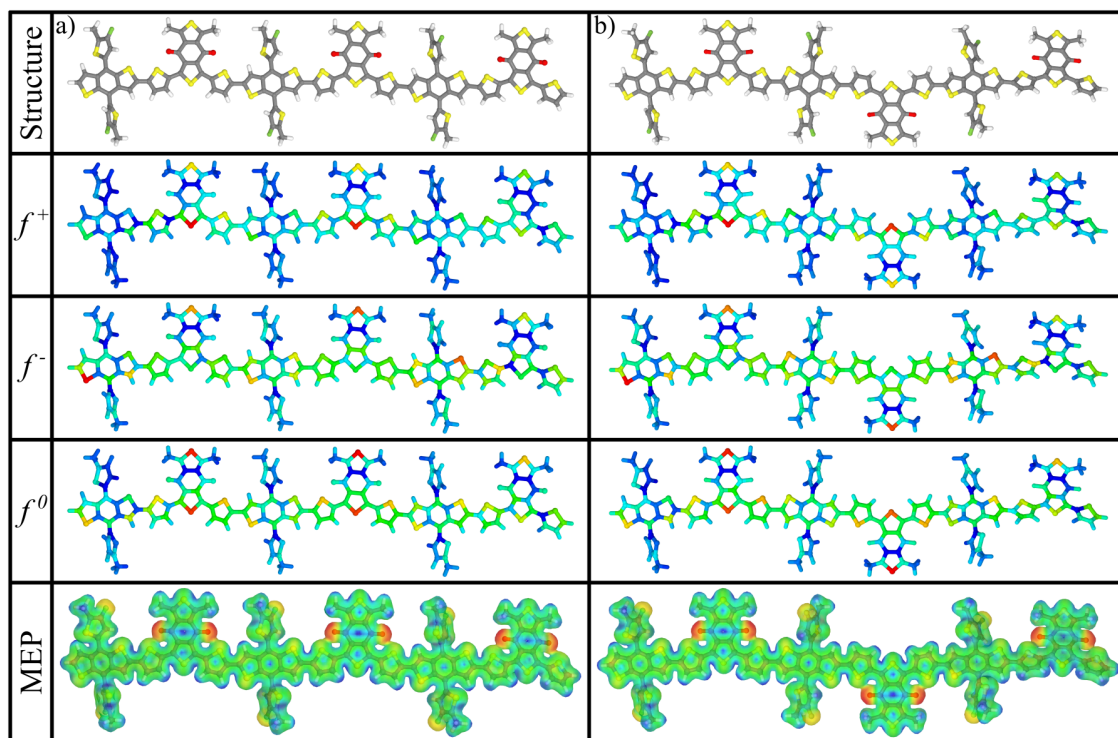
Source: Author.

Figure 1.25. CAFI and MEP results for PM6-2mer, a) straightforward and b) alternating.



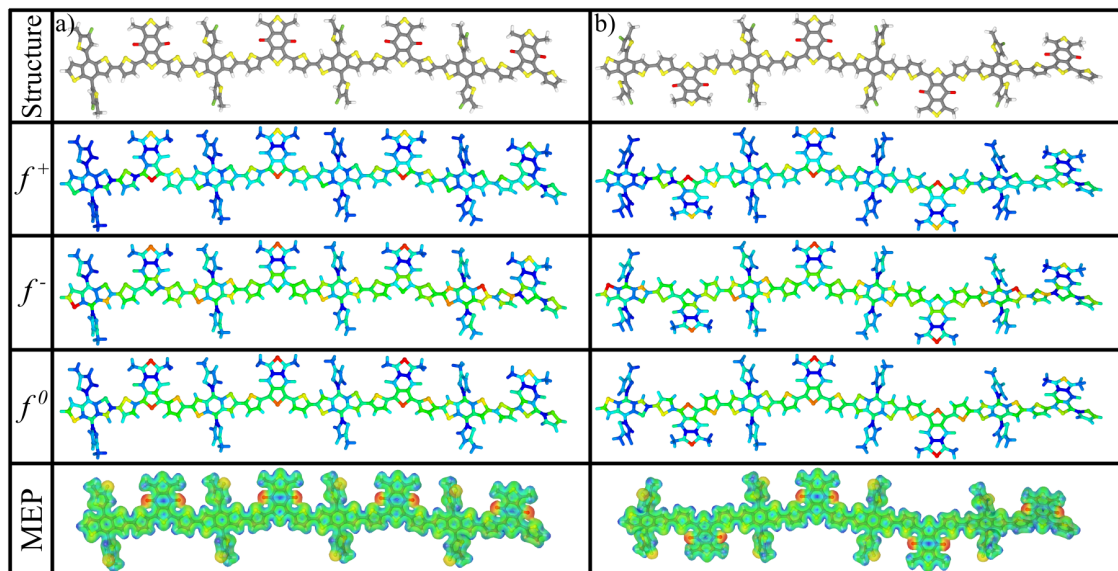
Source: Author.

Figure 1.26. CAFI and MEP results for PM6-3mer, a) straightforward and b) alternating.

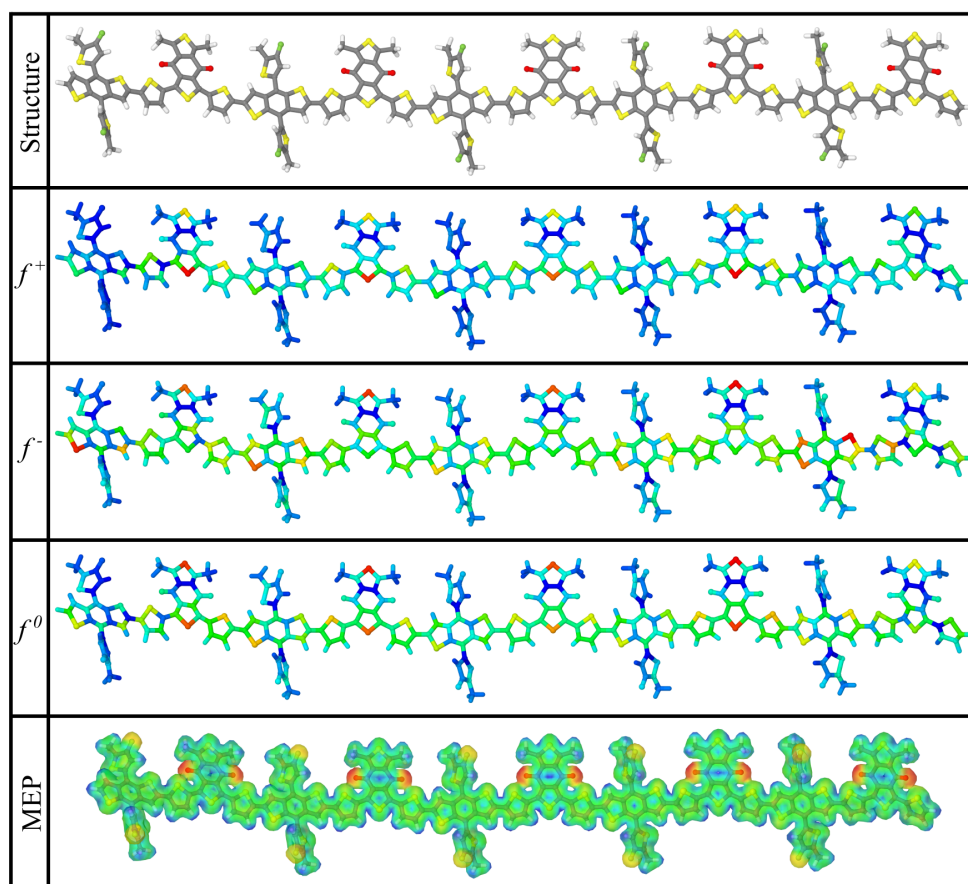


Source: Author.

Figure 1.27. CAFI and MEP results for PM6-4mer, a) straightforward and b) alternating.

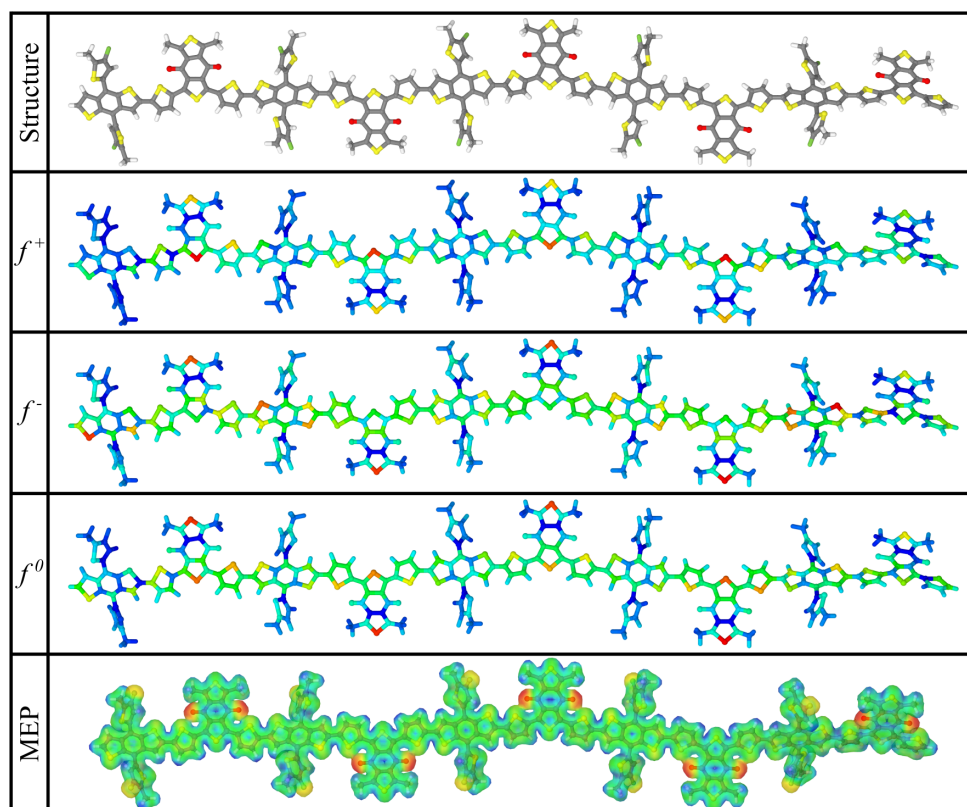


Source: Author.

Figure 1.28. CFI and MEP results for PM6-5mer.

Source: Author.

Figure 1.29. CFI and MEP results for alternating PM6-5mer.



Source: Author.

The first noticeable feature from PM6-1mer is its electron acceptance capability, presenting many highly reactive f^+ sites. Said sites are, in reactivity order, the bottom and top S atoms in the thiophenes bonded to the cyclohexanedione block, and the S atom in the terminal thiophene ring (right side of the Figures). Its electron donation ability (f^-) is concentrated in a single atom, the S atom from the leftmost thiophene unit of the Figure. Regarding the MEP, negative potential is shown in the cetones, which is good for the f^- sites and may enhance its electron acceptance ability.

The results for more extended oligomers show an interesting feature of PM6, as its reactivity towards electrophilic agents increases significantly as it grows in size. This is a very different behavior from D18-*n*mer, which had presented basically the same f^- from the monomer to the last calculated structure. For bigger PM6 oligomers, the f^- sites are interesting, the first unit (left to right) kept the very reactive leftmost thiophene's S atom, this reactive site gets less reactive towards the center, and more reactive as it approaches the right corner. While in the rightmost unit, the other thiophene bonded in the cyclohexane also gets its S atom reactive. In summary, these S atoms are more reactive in the corners than in the

middle portion, suggesting a possible border effect. On the other hand, as it grows, PM6 gets new reactive sites in the form of the top S atom from the cyclohexanedione bonded thiophene. These sites are more reactive in the center, as it can be noticed that its leftmost iteration is slightly less reactive, and the rightmost iteration is basically inactive. To summarize, the average f^- increases with its size, some sites are more reactive in the center, while others are more reactive in the corners, in other words, PM6 has good donor characteristics, as regarding its CAFI values.

Interestingly enough, an opposite effect happens to f^+ , as the number of highly reactive sites per units reduces to 1 (0 for the rightmost unit), the lower S in the thiophene bonded to the cyclohexanedione (the most reactive for PM6-1mer). It has become clear that PM6 loses a lot of its acceptors capability as it grows bigger, which is a good feature for its general purpose in an OSC.

The MEP still doesn't show a relevant role to help PM6 be a good electron donor. As it is the same in all sizes, it still just may be helping f^+ interactions (electron acceptance capability). Moreover, similarly to D18, this discussion offers insights on the possible stacking. The big difference here is that PM6 films do not present as good crystallinity as D18, however they do present a π - π face on stacking (YUAN et al., 2019; ZHU et al., 2022). Regarding MEP insights, it is expected that the negative charges in the O atoms will repel each other in the stacking structure, therefore vertical or sideways shift is to be expected in PM6 domains, just like in D18. In the case of PM6 the vertical shift is important as it allows the sites for electron donation and acceptance sites to be closer to each other.

In conclusion, PM6's results are similar to D18's: it presents a strong donor character but also shows ambivalent behavior for charge transport. In addition, the alternating units do not affect the reactivity, therefore a highly disordered polymer isn't a problem.

Beyond this discussion, comparing and combining previous results (D18's and Y6's results), and their reported PCE it is possible to have a better understanding of why D18 was a more successful system (WEI et al., 2020). In general, researchers have already highlighted the importance of Y6's ambivalent charge transference and that it is possible to find Y6 molecules in the donor domains after spin coating and thermal annealing, here it can be seen that this characteristic is also present in the donor material (ZHANG et al., 2020; ZHU et al., 2020a, 2020b). It seems that one important component to achieve high PCE (at molecular scale) is the existence of an ambivalent charge transfer feature. This is very important as it would lead to less electron/hole getting trapped in an acceptor/donor in its opposite domain. Our data suggest that D18 has stronger donor capability, while being a good acceptor, and

also having the same site to both receive and donate electrons, *i.e.*, in a thin film/crystal structure charges can move easily between different D18 oligomers.

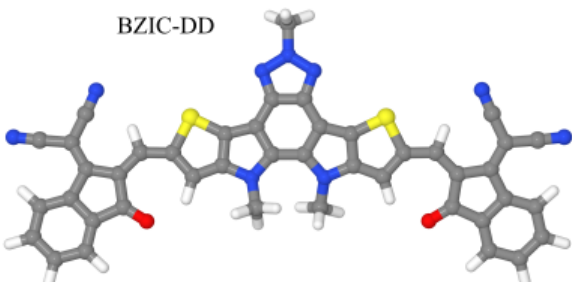
1.3.4. BZIC STUDIES

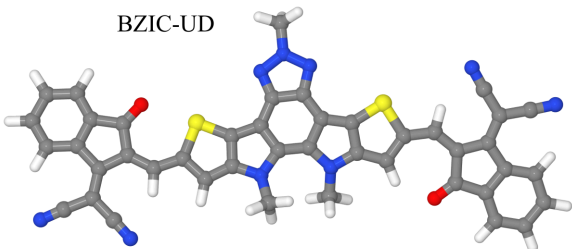
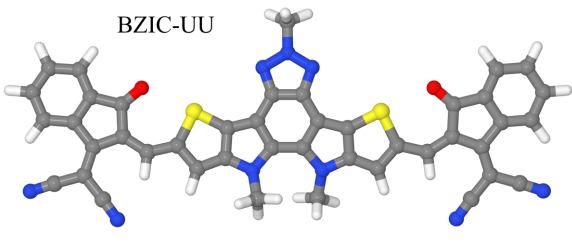
As mentioned in the Introduction and in Materials and Methodology sections, other than the successful PM6:Y6 and D18:Y6 donor:acceptor pairs, there's also interest in conducting a comparative study involving older and less effective pairs. The pair selected for this purpose is the HFQx-T:BZIC one. In this section we are going to focus on the acceptor, BZIC. This molecule was the one to introduce the A-DA'D-A type NFA by Feng L. *et al* in 2017 (FENG et al., 2017).

1.3.4.1. STRUCTURAL STUDIES

As an acceptor, BZIC structural studies are quite similar to those of Y6. The BZIC initial structure was built as shown in Figure 1.4. Similarly to Y6, no alkyl side chains are taken into consideration. Moreover, it's noticeable that unlike Y6, BZIC's EG have been reported in different positions (one upwards and the other downwards, and both pointing upwards) (FENG et al., 2017; LU et al., 2021; WEI et al., 2020; YUAN; ZOU, 2022). Given its symmetric shape, it doesn't matter which side is up and which is down, moreover, it could be possible to have even both down. To gauge this possibility, three BZIC conformers were made: BZIC-DD (both EG pointing downwards), BZIC-UU (both EG pointing upwards) and BZIC-UD (one EG to each direction). Table 1.6. brings the optimized structures and energetic information for the three conformers.

Table 1.6. 3D structure, total energy, FMO energy and ΔE_{LH} for BZIC conformers.

3D structure	Energy related information (eV)	
	Total energy	-84103.056
	E_{HOMO}	-5.586
	E_{LUMO}	-3.474
	ΔE_{LH}	2.111

	Total energy	-84103.070
	E_{HOMO}	-5.557
	E_{LUMO}	-3.448
	ΔE_{LH}	2.109
	Total energy	-84103.081
	E_{HOMO}	-5.530
	E_{LUMO}	-3.422
	ΔE_{LH}	2.108

Source: Author.

In relation to the structure, all three BZIC showed similar planarity, where the core is in one plane and both EGs are slightly off plane in opposite directions. Such an effect is also noticed in Y6.

Energetic wise, they are all very similar. Note that the most stable one (with the lowest total energy) is BZIC-UU. However, once $\Delta E_T \sim kT$ (UU to DD) it's acceptable to use any of the three conformations in this study. Moreover, their FMO energies are quite similar which implies that in a bulk, or film, composition they would be energetically indistinguishable.

To better evaluate the electronic similarity of these conformers, and considering that their calculations are relatively cheap, we've decided to evaluate the CFI and MEP for all three structures. Doing so, we're able to check if there are any significant differences in their properties other than the purely energetic ones.

One property that clearly has to differ is the molecular dipole moment, since most of it comes from the EG position. And in fact it does, Table 1.7 shows the molecular dipole moment for each conformer.

Table 1.7. Dipole moment results, in Debey (D), for Y6s and their dimers.

Structure	Dipole moment (D)
BZIC-DD	10.177

BZIC-UD	2.708
BZIC-UU	5.809

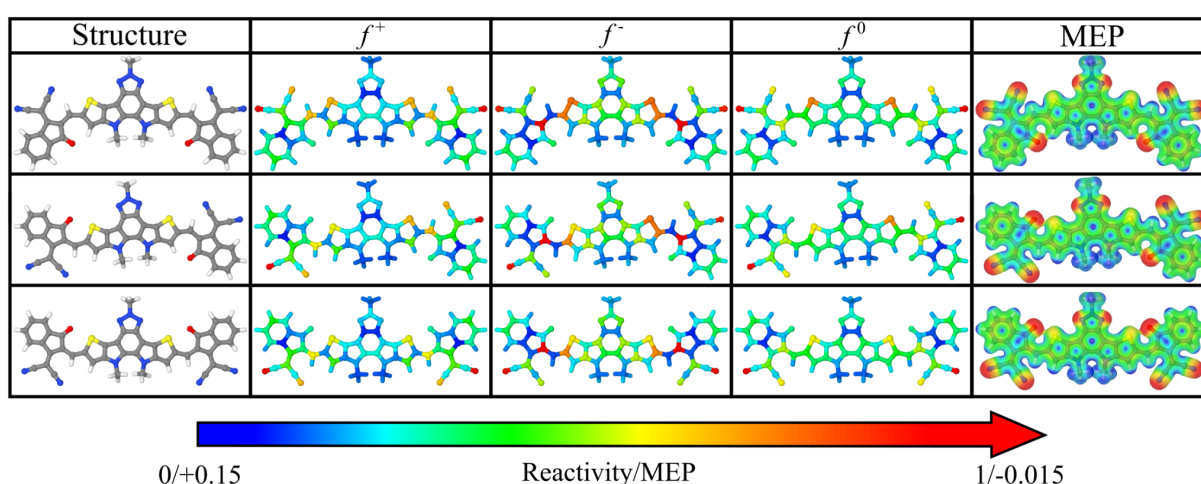
Source: Author.

Note the values are way higher than the ones noticed for Y6, even in the absence of the alkyl side chains. BZIC-DD's and BZIC-UU's dipole moment are in opposite directions, the first points downwards (similar to Y6) whilst the second points upwards. Depending on the effect dipole moment has in the charge movement, these conformers can act very differently. Moving to BZIC-UD, its dipole moment points towards the upwards EG. Considering that the dipole moment could affect charged particle movement, BZIC-UD's dipole sets a preference to one EG direction, while the others are more generic "to the EG" or "to the core" preference.

1.3.4.2. CAFI AND MEP RESULTS

As mentioned above, all three BZIC conformers were considered for CAFI and MEP calculations since they're all possible structures and CAFI and MEP calculations are cheap enough. Therefore it is possible to investigate if flipping EGs has any effect on these properties and Figure 1.30 illustrates these results.

Figure 1.30. CAFI and MEP results for BZIC's different conformers.



Source: Author.

Not much of a surprise to notice that CAFI is almost identical in all three BZIC. The difference comes in the torsion between EG and core, in fact the cause of distinction between

them. Namely, it's the S atoms and the C connecting EG to the core, if they are next to a downwards (upwards) EG they get more (less) reactive. This effect is stronger in f^- , however any of these sites are the most reactive in any indexes. Although this effect sets BZIC-DD as most reactive out of the three, it may not be of much relevance, since there are other sites of greater reactivity.

In a general sense, BZIC shows greater reactivity for f^- , showing an interesting donor characteristic. As sites for most likely electron donation it shows the C in EG connecting to the C bonding it to the core and the lower N from the EGs. The thiophenes also show themselves as reactive sites mainly on S and edge C atoms (if next to a downwards EG). On the other hand, as sites for electron acceptance (f^+) it shows only the lower N atoms in the EGs. The other EG's N, C connecting core and EG and S atoms show medium/high reactivity.

In relation to the MEP, comparatively they are the same for all the conformers. It's also similar to Y6's MEP. It's noticeable that the charge difference from most negative to positive is higher than for Y6 (hence higher dipole moments). Also, the negative charges in the nitriles may attract electrophilic agents, and interaction might actually happen as indicated by its f^- , improving its donor capabilities.

In conclusion, BZIC results for CFI and MEP are rather similar to Y6's, as to be expected, once Y6 came from BZIC modifications (SHOAEE et al., 2023; YUAN; ZOU, 2022). The greatest difference is in the electron deficient core (-DA'D-), as the Y6's S atom there is really important for all CFI. Not surprisingly, BZIC is classified as an worst acceptor and a better donor than Y6. Results until this point are showing that both donor and acceptor materials should have donor and acceptor capabilities, BZIC-based OSC might've not been as successful because BZIC's weak electron acceptance compared to its own electron donation capability (FENG et al., 2017; WEI et al., 2020).

1.3.5. HFQX-T STUDIES

As previously mentioned, the pair HFQx-T:BZIC was selected for its position as the first NFA-based OSC. In this section we are going to focus on the donor, HFQx-T.

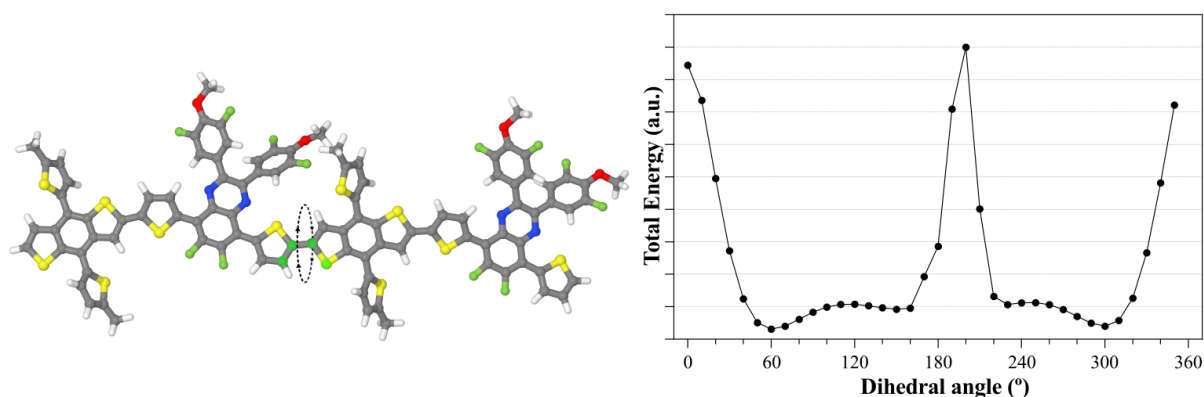
1.3.5.1. STRUCTURAL AND SATURATION STUDIES

Here the HFQx-T studies in relation to its conformation and size are presented. As mentioned in Section 1.2.2.2., this polymer has by far the most computationally demanding monomer due to its complexity and many rotating rings resulting in a number of degrees of

freedom (even without its alkyl side chains). All this complexity demanded specially careful monomer building. This process was very meticulous and quite long; details regarding it are presented in Appendix H, herein the usual dimer dihedral investigation and Meier's saturation study was applied.

Following the previous polymer studies, different units of HFQx-T are named HFQx-T-*n*mer. As usual, the first thing to do now is to find out the best dihedral angle between two units of HFQx-T. Figure 1.31 shows how the scan was made and the obtained results.

Figure 1.31. HFQx-T dihedral scan study; green highlighted atoms indicate the atoms composing the scanned dihedral angle. 0° are related to conformations involving S atoms of the terminal thiophene rings at opposite sides.

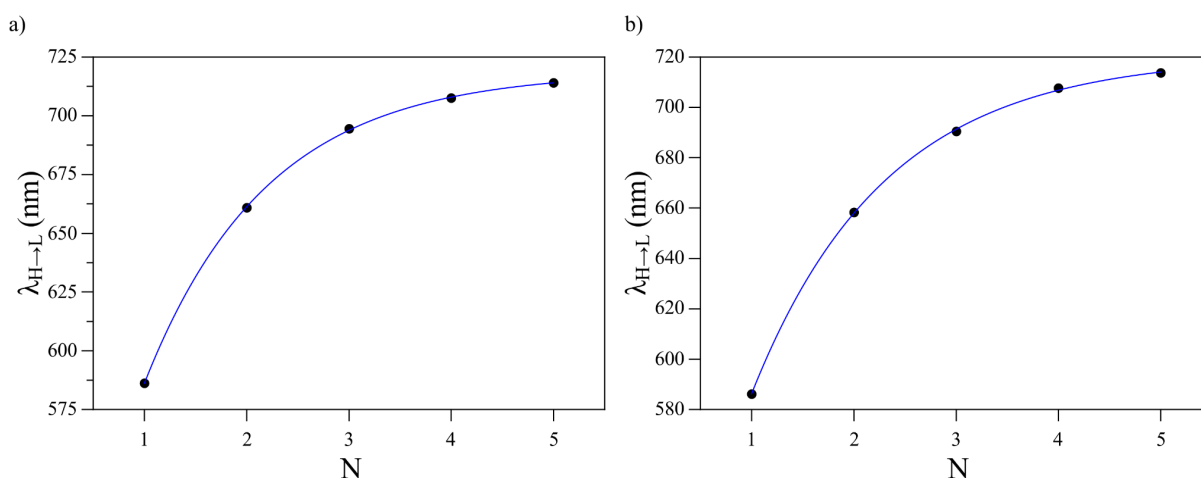


Source: Author.

From this study the dihedrals (after optimizing) responsible for the smallest total energy are $\sim\pm 22^\circ$ and $\sim\pm 161^\circ$, for straightforward and alternating structures, respectively. It is important to highlight that these in-between dihedral angles are allowed to change, unlike the internal rings dihedral angles, that were actually frozen for optimization (Appendix G).

Next are the findings from Meier's saturation study, Figure 1.32 and Table 1.8 show these results.

Figure 1.32. HFQx-T Meier's fit result for structures with (a) straightforward and (b) alternating structures.



Source: Author.

Table 1.8. Meier's equation data on HFQx-T saturation.

	straightforward	alternating
a	0.837	0.766
dλ (nm)	132.59	134.09
λ_∞ (nm)	718.70	720
n_{ef}	6.8	7.4

Source: Author.

The HFQx-T's complex structure also appears to be a problem for obtaining saturated oligomers, as its $n_{ef}=6.8$ and $n_{ef}=7.4$, for straightforward and alternating structures, respectively. This is much bigger than the previous polymers, and much more problematic considering its complexity. The biggest size possible to calculate for Meier's approach was HFQx-T-5mer, two units shorter than the saturated oligomer. However, it is important to highlight that saturation via ΔE_{LH} happens for HFQx-T-4mer, meaning that between 4 to 5 units the $\Delta E_{LH} < kT$, for both types of structures.

These results have defined the HFQx-T as a very complex system, whose saturation couldn't be achieved considering the Meier's criteria. Conversely, the oligomer saturation was achieved considering the energetic variation ΔE_{LH} , from which four units are already

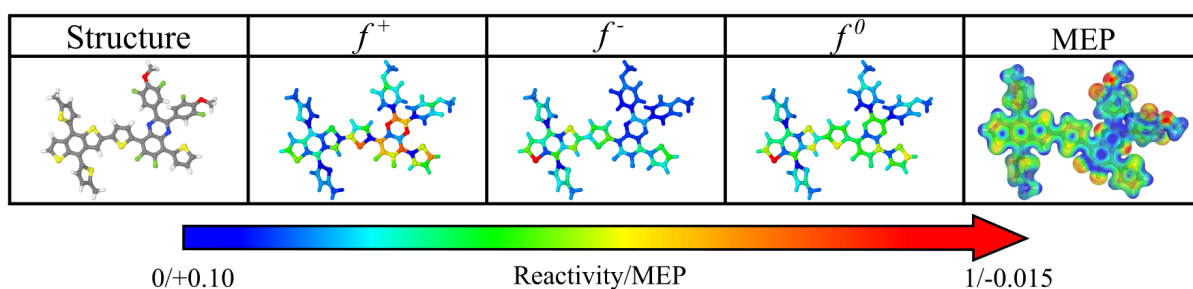
saturated. In this sense, the CFI and MEP calculations for this polymer were made up to HFQx-T-5mer, for both structures.

About its conformation itself, it is noticeable that this compound is not as planar as previous polymers, presenting a little bending on its longitudinal axis, as usual, but also showed torsion in this very axis. Even using alternating positive and negative dihedral angle values weren't enough to eliminate this effect, however helped to mitigate it.

1.3.5.2. CFI AND MEP RESULTS

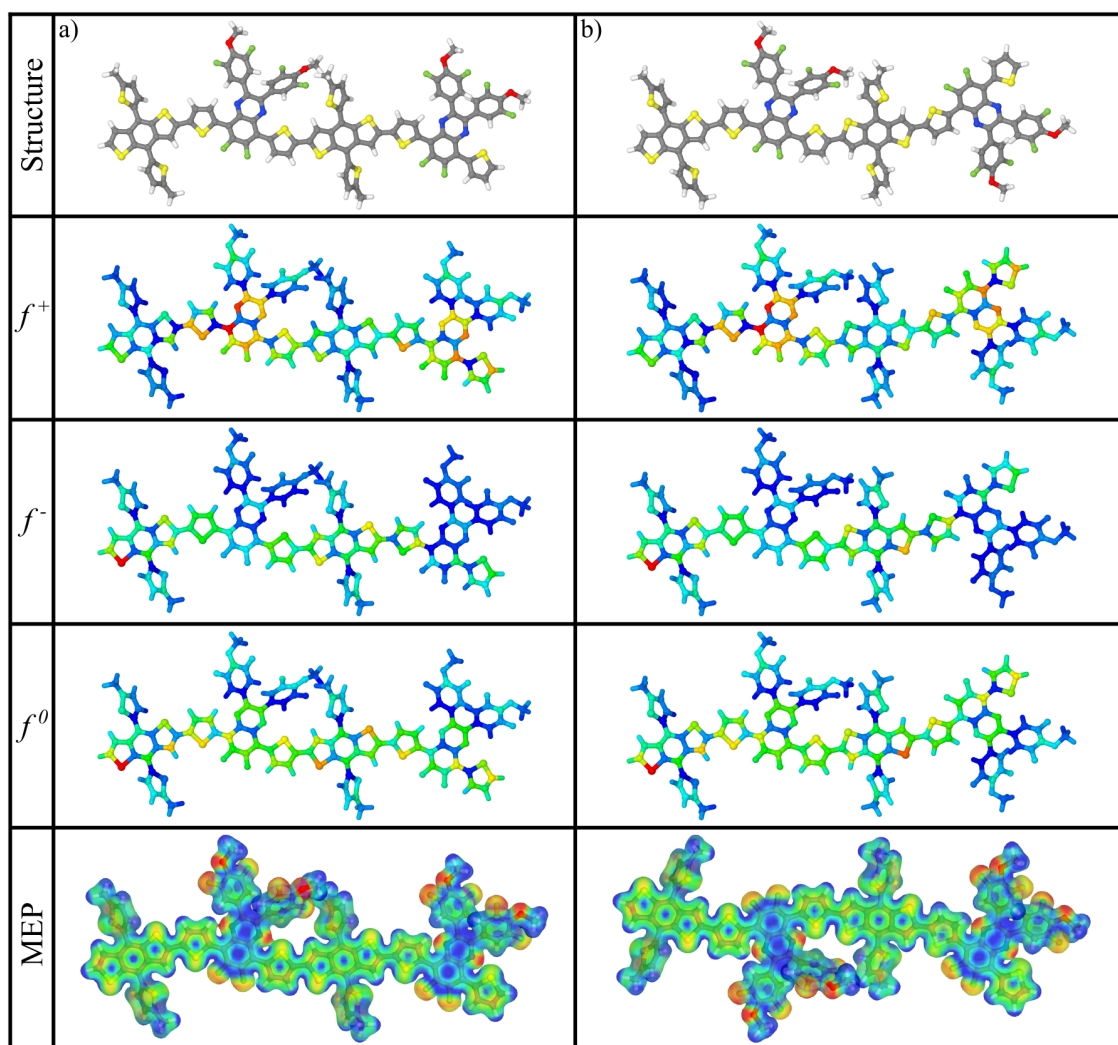
As mentioned above, structures from one to five units, straightforward and alternating, were considered for CFI and MEP. The results for all studied HFQx-T's structures are shown by Figures 1.33. to 1.38.

Figure 1.33. CFI and MEP results for HFQx-T-1mer.



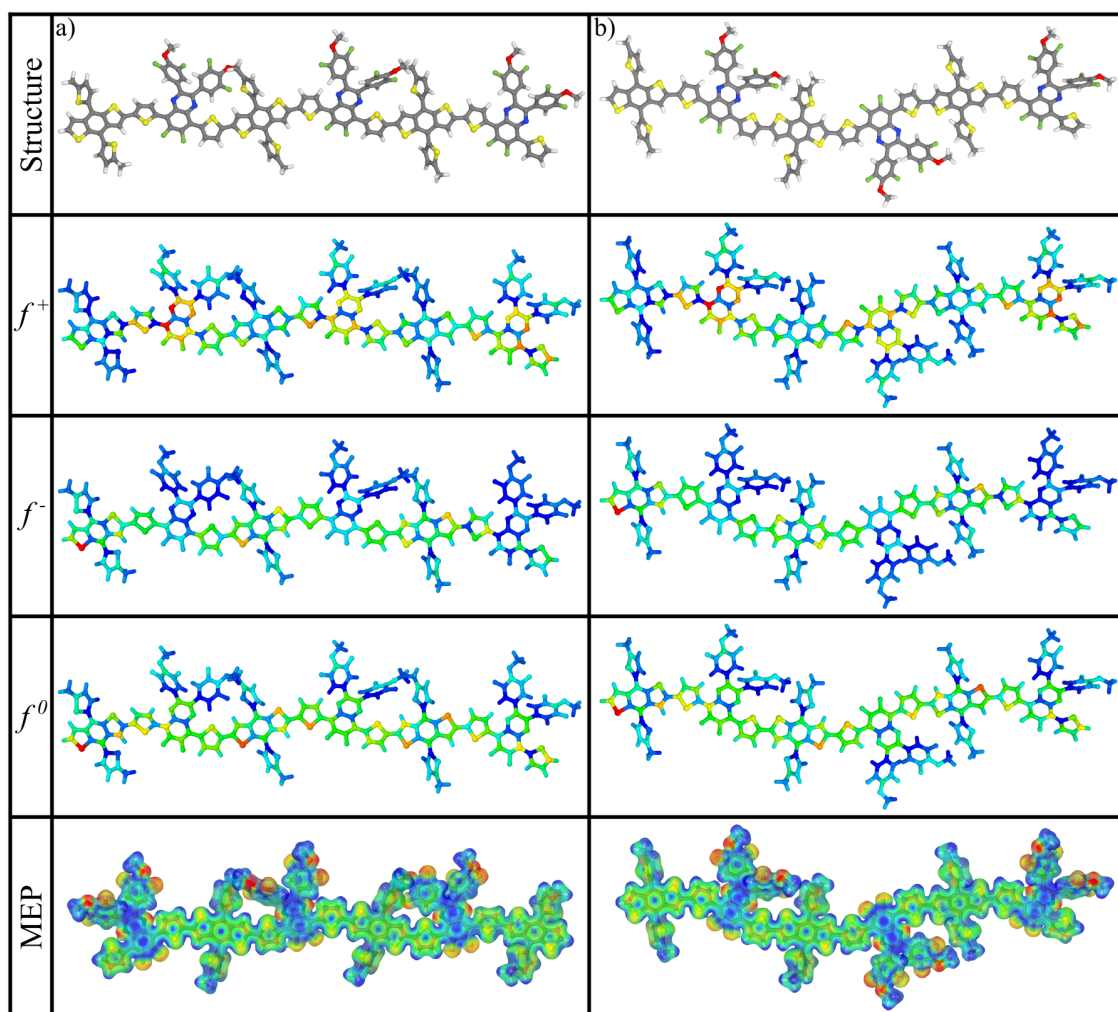
Source: Author.

Figure 1.34. CAFI and MEP results for HFQx-T-2mer a) straightforward and b) alternating.



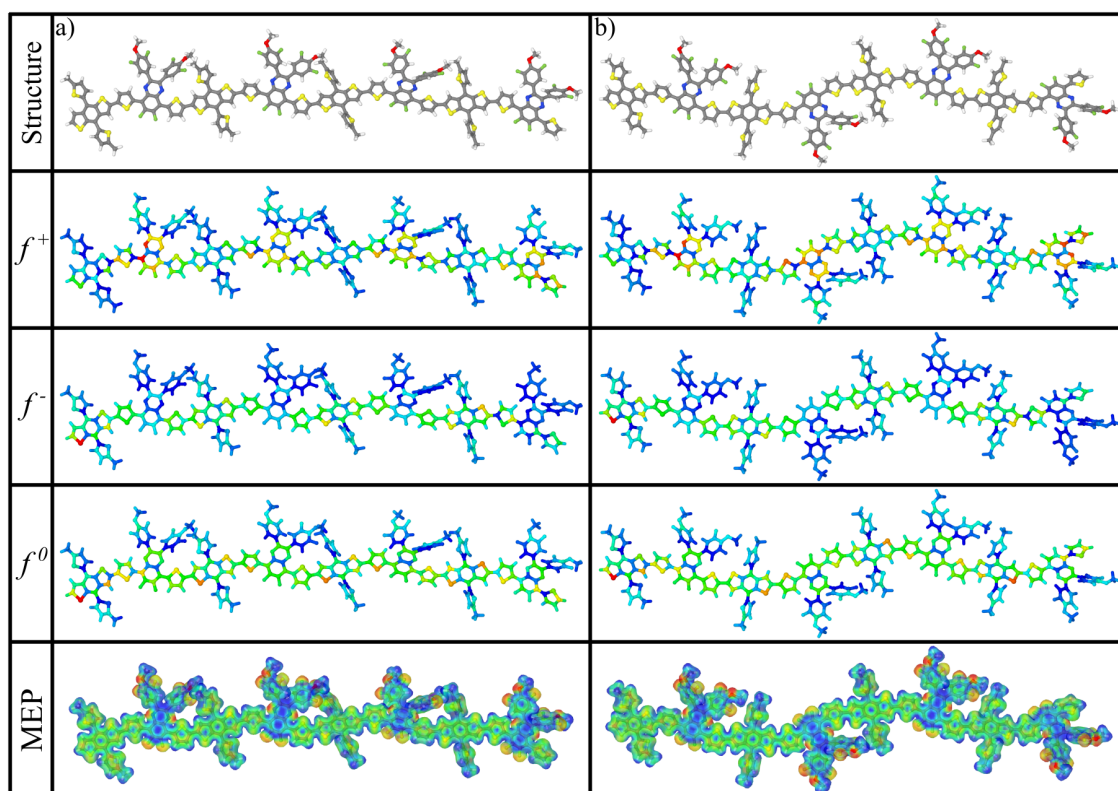
Source: Author.

Figure 1.35. CFI and MEP results for HFQx-T-3mer a) straightforward and b) alternating.

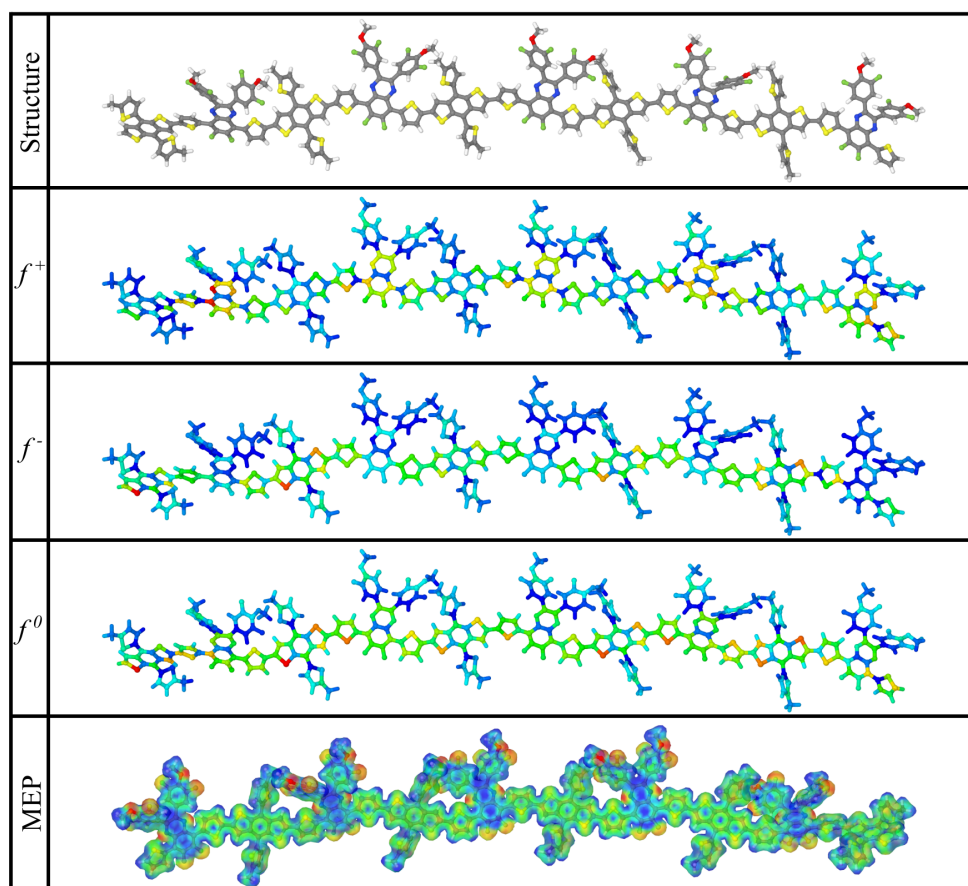


Source: Author.

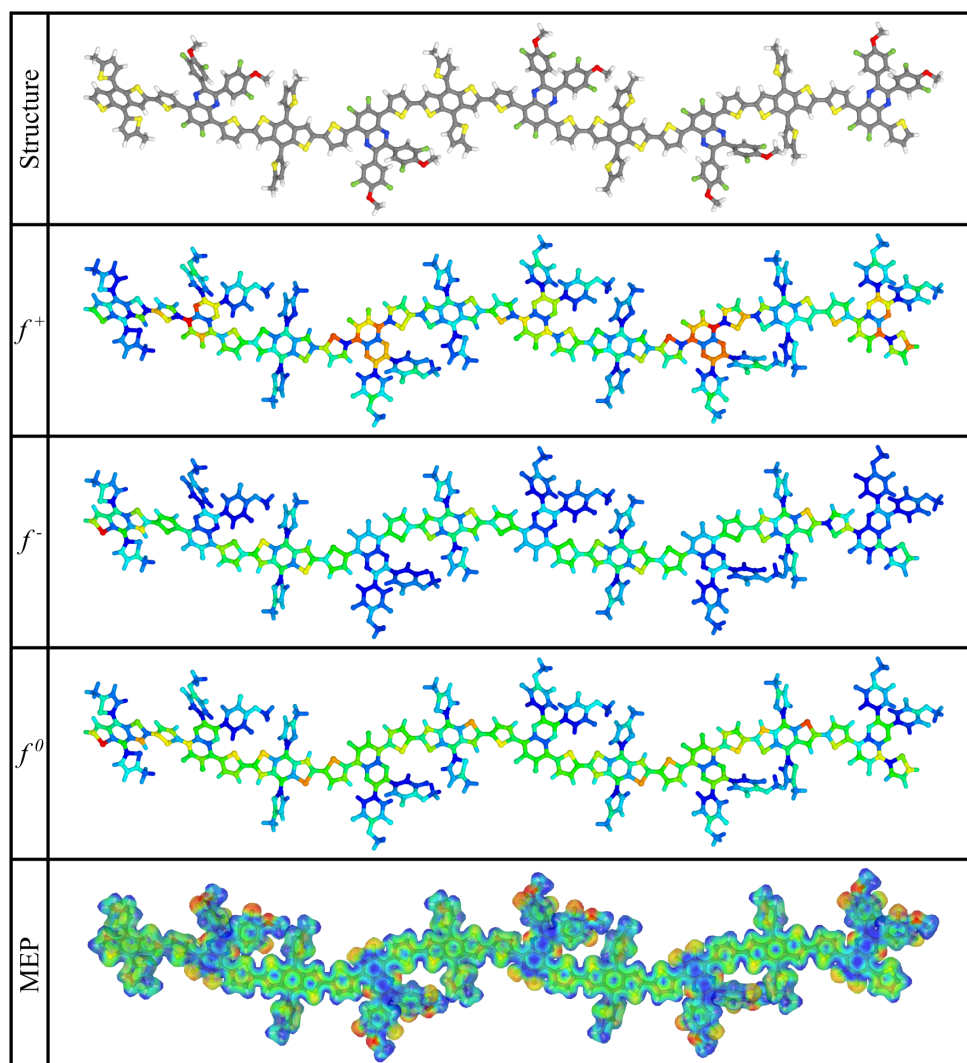
Figure 1.36. CFI and MEP results for HFQx-T-4mer a) straightforward and b) alternating.



Source: Author.

Figure 1.37. CFI and MEP results for HFQx-T-5mer.

Source: Author.

Figure 1.38. CAFE and MEP results for alternating HFQx-T-5mer.

Source: Author.

Starting with the MEP, as shown numerically in the scale and evidenced by the amount of blue color in the figure, HFQx-T is more positively charged than D18 or PM6. This positive charge is mainly concentrated on the rings of the main chain. Interestingly enough, most negative areas are also centered on the ring structures, at the N and O atoms. It's desirable to have negative (positive) potential close to f^- (f^+) to take advantage of the electrical force.

The CAFE results resemble a bit of the PM6 behavior, in the sense that its monomer shows weak f^- and strong f^+ , which is an acceptors characteristic. For PM6 this behavior is quickly abandoned, as in its 2mer it's already possible to see a great enhancement in its donation capabilities (better f^-). However, that's not the case for HFQx-T, which keeps a strong f^+ to all calculated structures. This characteristic seems harmful, the weak f^- could

make this material work as an electron trap and hinder the electric current and overall PCE. In addition, it is noticeable that most of its donor character from bigger structures could be attributed to border effects.

Moreover, the combination MEP+CAFI shows more advantage towards electron acceptance, as positively charged regions (attract negatively charged sites) are close to sites with strong f^+ (electron acceptance sites). This combination with the observed torsion and quantity of rings, hinders molecular interactions; in particular these features should lead to lower π - π stacking and reduced FF in relation to the other polymers. In fact that is observed in experimental studies, with neat HQFx-T showing hardly any π - π stacking X-ray scattering (ZHOU et al., 2018) and smaller FF than D18 and PM6 (FENG et al., 2017; WEI et al., 2020).

It is important to highlight that strong border effects are noticed, since the edges are quite more reactive than the main body. This is likely due to its reduced size, hence the importance of Meier's results. However, even ignoring the highly reactive edges, it is noticed that in the main body the reactive sites for f^+ are inert for f^- , and vice versa. This lack of superposition of CAFI sites gets in the way of intermolecular charge transfer. Finally, this time it is noticed higher reactivity sites for alternating structures in comparison to the straightforward ones.

To summarize, using CAFI and MEP as tools to investigate HFQx-T it was possible to trace the characteristics that set it as a worst donor than D18 and PM6. The main points were: structure and charge distribution that hinder the stacking; stronger acceptor character; hard to pair f^- and f^+ sites, hindering intermolecular charge-transfer; charge distribution that enhances electron acceptance instead of donation with strong acceptance CAFI.

1.3.6. PCBM STUDIES

PCBM is the fullerene-based acceptor that is used here as a comparison parameter for Y6 and BZIC molecules, which are NFAs. Not only PCBM, but also other fullerene-based materials, have attracted attention in the OSC field due to their high electron mobility due to their spherical shape (LI; YIP; JEN, 2012; WEI et al., 2020). Despite it, this class of materials was abandoned as sole acceptors for OSC due to their weak visible light absorption and poor morphology stability, being swapped for the NFAs (WEI et al., 2020; YU et al., 2019). More recently, fullerene-based materials made a comeback as an additive on ternary (one donor, 2 acceptors) OSC, where a small portion of the active layer is composed of a fullerene-based

acceptor. For instance, it was reported a PM6:Y6:PC_nBM ($n=61$ or 71) on a weight to weight ratio (w/w) of 1:1.2:0.2 with enhanced FF and PCE in relation to PM6:Y6 OSC (GAO et al., 2020; PAN et al., 2019; WEI et al., 2020; YU et al., 2019; YUAN et al., 2019). Herein PCBM structure and properties are studied in relation to its use as an acceptor in a D:A OSC.

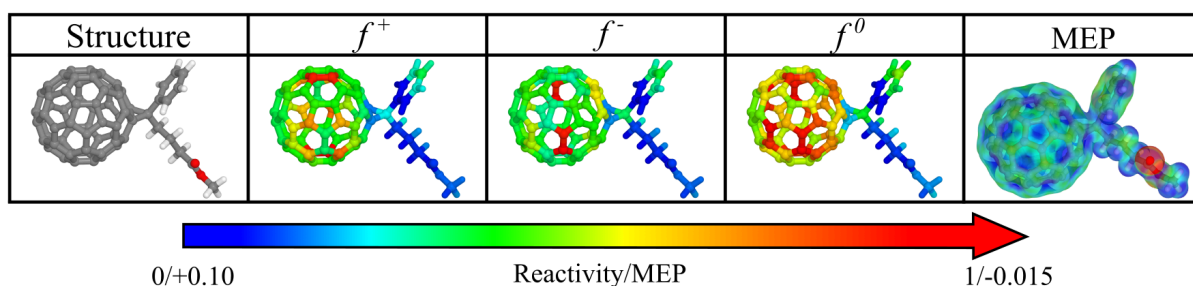
1.3.6.1. STRUCTURAL STUDIES

A fullerene can show up in multiple sizes, PCBM is a derivative of C₆₀ fullerene, sometimes named PC₆₁BM to differentiate from PC₇₁BM. This molecule's structural study started a bit different from the others, although it might look difficult to design it, Gabedit software and its great fragment substitution tool made it an easy task to achieve (ALLOUCHE, 2011). Unlike the other studied molecules, here no simplifications or conformer investigation were required, it's a pretty straight forward molecule to study. PCBM was simply designed and optimized in the described framework.

1.3.6.2. CAFI AND MEP RESULTS

With the usual set of tools, PCBM's CAFI and MEP were calculated and are displayed in Figure 1.39.

Figure 1.39. CAFI and MEP results for PCBM.



Source: Author.

In a general view of f^+ and f^- it's possible to notice that both have the same amount of very reactive (red) sites, however the overall reactivity for f^+ is higher since it shows other medium-high sites that are not present for f^- . It is also important to highlight that the most reactive sites are in pairs and on opposite sides of the fullerene. Depending on how these sites are aligned, charge transportation can be enhanced.

Having stronger f^+ than f^- shows greater acceptor character than a donor one, which is aligned to the role PCBM is expected to have. Also, the presence of highly reactive f^- sites

highlights the donor capabilities of PCBM, which is actually an important characteristic noticed for Y6.

In terms of MEP there's not much to be talked about, the fullerene part of the molecule is all around neutral on the atoms and positive in the regions without atoms. The areas with more negative MEP are located at non-reactive sites, which suggests the MEP has very little effect on helping positive charge transfer. The positive regions in the fullerene, on the other hand, can be of help as it can possibly attract negative charges next to highly reactive f^+ sites.

In summary, the PCBM area responsible for the charge transportation is the fullerene itself, and how effective it'll be is most likely tied to how well the reactive sites are aligned in the bulk. The most optimal stack is such that f^+ and f^- are aligned, which might allow the formation of a 3D network for charge transportation, similar to Y6. In the analyzed molecular scale properties, PCBM doesn't look problematic, actually seems quite promising, the problem however must rise in the stacking of this material and/or its interaction with P3HT or other donor polymers. An possible evidence of PCBM's qualities is the aforementioned use in ternary PM6:Y6:PCBM OSC, however it's said that its contributions lies in enhancing the morphology and widening of the absorption spectra (to harvest more photons) (WEI et al., 2020; YUAN et al., 2019).

1.3.7. P3HT STUDIES

PCBM is famous for its pairing with P3HT, building a widely studied P3HT:PCBM OSC. In this section details about P3HT's structure and properties in relation to its use as an OSC donor material are discussed.

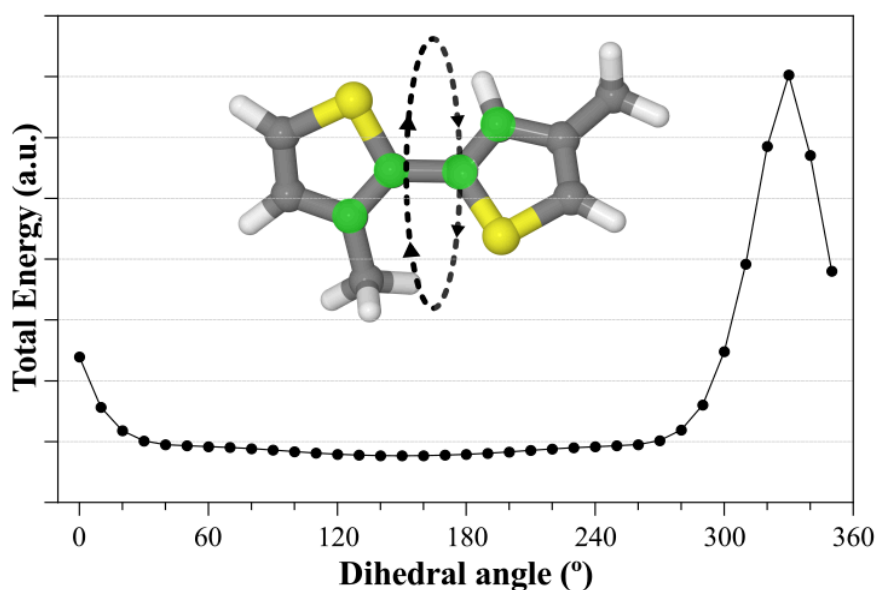
1.3.7.1. STRUCTURAL AND SATURATION STUDIES

P3HT is by far the simplest donor material in this study, its main body is one thiophene, that can be found eight of in the monomer of PM6. A study from Batagin-Neto *et al* already applied Meier's saturation studies for this material where they've found a conjugation length of 21 units (BATAGIN-NETO et al., 2013). A high n_{ef} was to be expected as the saturation is tied to the size of the π system.

The study of Oliveira and Lavarda on P3HT in a molecular dynamics approach showed that the polymer assumes alternating structure with 5° to 65° angles between the monomers plane (DE OLIVEIRA; LAVARDA, 2013). It must be addressed that these studies were made considering the alkyl side chain of P3HT, which is not the case for this work.

Considering the framework of choice, where it was opted to dismiss alkyl side chains, a test had to be made to gauge the dihedral angles between two units. The usual scan for dihedral angle was made, as done for the other polymers, and the results are presented in Figure 1.40.

Figure 1.40. P3HT dihedral scan study; green highlighted atoms indicate the atoms composing the scanned dihedral angle.



Source: Author.

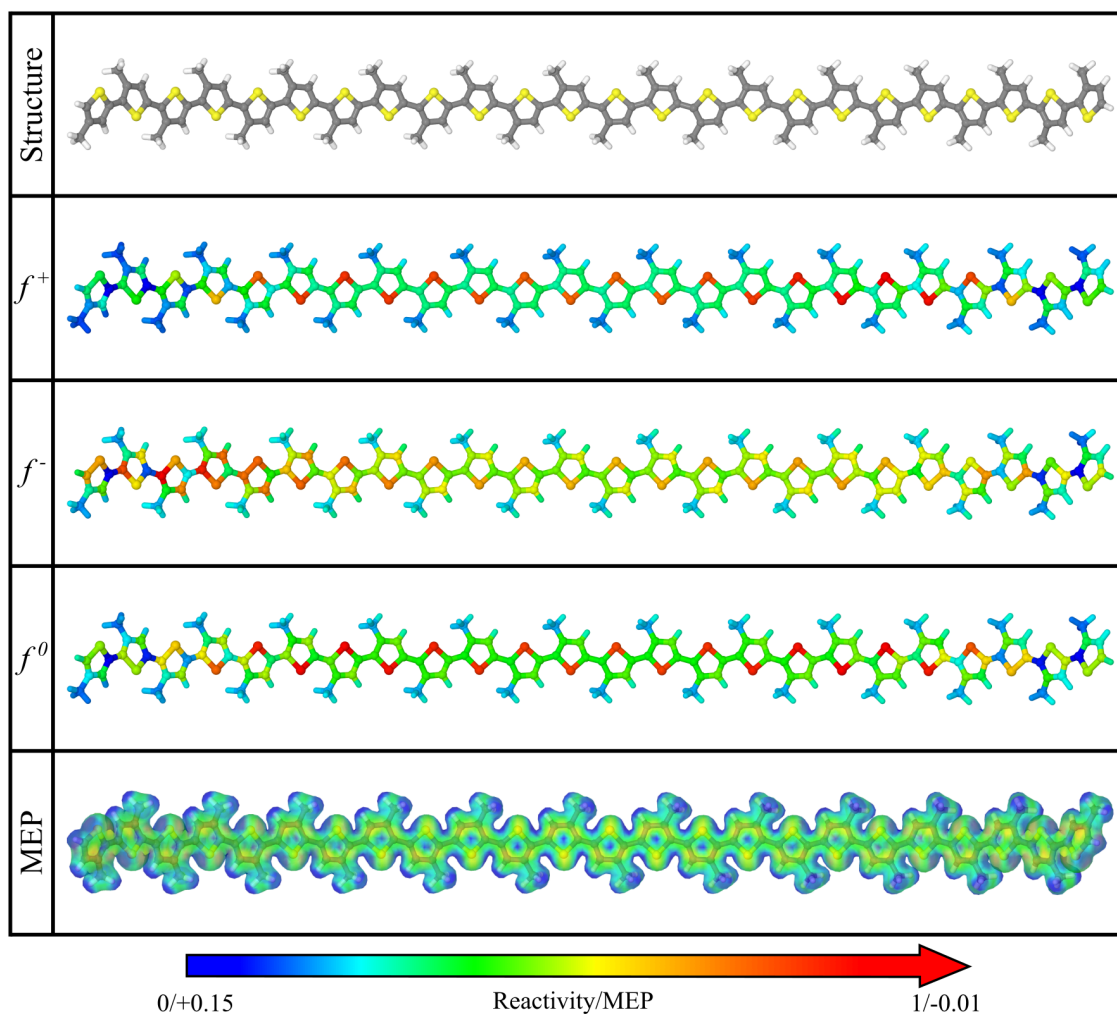
From this study we've found that angles around 160° was a good point to start, which agrees with the published result of an alternating structure (DE OLIVEIRA; LAVARDA, 2013). Optimizing a P3HT-2mer structure with this dihedral angle leads to a final structure of ~150° angle. This angle is also in the range observed by Oliveira and Lavarda (DE OLIVEIRA; LAVARDA, 2013).

As saturation study in the approach has already been made and published, the structure P3HT-24mer was directly made (considering previously calculated dihedrals, and in a slightly bigger than saturation length, similarly to PM6 and D18 final structures) and optimized. CFI and MEP were then estimated. From the optimization it can be noticed that, as expected of a long polymer, P3HT-24mer showed a bend in its longitudinal axis due to entropy forces. Moreover, its initial dihedral of ~150° found in P3HT-2mer is optimized to ~165°, making it a less twisted structure.

1.3.6.2. CAFI AND MEP RESULTS

Considering the obtained P3HT-24mer structure, the CAFI and MEP were calculated and are displayed in Figure 1.41 with the color scale for both results.

Figure 1.41. CAFI and MEP results for P3HT-24mer.



Source: Author.

From CAFI results it is clear that P3HT has a better donor than acceptor capabilities due to its overall higher reactivity in f^- . What is deceiving about these results is that in the middle of the molecule f^+ has more red sites, therefore appears as having better acceptor character. The reason behind this are the border effects, as it can be noticed unusually high reactive sites in the leftmost corner of f^- , which hinders the middle sites as everything is normalized. If border effects are eliminated, it could be expected to have even more reactive

(more red and orange) sites in the middle of f^- . This consideration actually does not affect its acceptor character as the border effect is unusually low reactivity sites. In general, P3HT shows good donor characteristics without damaging its acceptor capabilities, which is a valuable feature in polymers like PM6 and D18. Moreover, the general higher reactivity on f^- might be significant for charge hopping through the polymer. Also, depending on how good the stacking is, the charge transfer between two units could be easy as even though the sites would not be aligned they might stay close to each other.

With MEP it is possible to see that this is a pretty neutral molecule with positive MEP at its H atoms. In each unit the C opposite to S has slightly negative MEP. In general this result brings one important piece of information, as S is always the reactive site of P3HT, the positive MEP helps attract negative charges, possibly enhancing its acceptor capabilities.

Overall CAFI and MEP indicates a good donor for OSC applications, with possibly good ambivalent charge transfer (good f^+ and better f^-) capability. What could have hindered its PCE is its problematic stacking, which does not show much face-on π - π stacking, and studies tried different approaches and techniques to enhance this characteristic (CHU et al., 2016; RUDERER et al., 2013; SCHOLES et al., 2017). Moreover, P3HT is well known for pairing up with PCBM which also didn't show the best of results as a good acceptor (see Section 1.3.6), therefore it does not help P3HT.

In conclusion, P3HT seems to be a good donor regarding its molecular properties, indicating that the poor PCE of P3HT:PCBM OSC is related to the interaction between the components and the stacking of themselves.

1.3.8. COMPARATIVE ANALYSIS

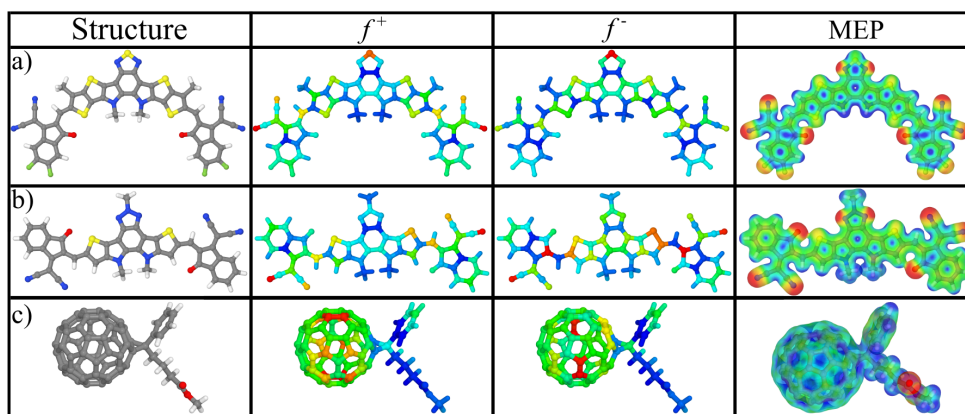
In previous sections some results were brought back in a comparative sense. In order to better organize and amplify this discussion, in this section the acceptor molecules will be directly compared, and so will the donor polymers, but only at their saturated conformations. These analyses set out to better understand and possibly pin-point the most important molecular characteristics of efficient materials for OSCs.

1.3.8.1. ACCEPTORS' CAFI COMPARATIVE ANALYSIS

The studied acceptor materials were Y6, BZIC and PCBM, defining a very efficient NFA, the first A-DA'D-A NFA (predecessor of Y6), and a fullerene-based acceptor, respectively. Figure 1.42 brings the MEP and CAFI results for these acceptors, f^0 is omitted

as only charge transfer related information is relevant for this discussion. Their color scale is of course the same as shown individually in each section, and different between them (i.e. it defines only intramolecular tendencies).

Figure 1.42. CAFI and MEP results for a) Y6, b) BZIC and c) PCBM.



Source: Author.

In general, strong acceptor/donor properties can be understood in terms of: *i*) the effective distribution of reactive centers over the molecule, and *ii*) the presence of highly reactive sites. The first feature indicates the existence of a large number of possible CT routes that are relevant for the percolative transport of electrons, however, it also distributes the reactivity over several centers, reducing their dominance compared to the inert sites. Conversely, the latter characteristic defines a very plausible route and leads to systems with reduced accessibility. In this context, these features must be well balanced to achieve effective acceptors/donor materials.

As discussed, not only does Y6 present these sought-after acceptor characteristics, but it also shows electron donation capabilities. Conversely, it can be easily noticed that BZIC (b) shows an opposite behavior. Its donor character is stronger than its acceptor one, presenting more highly reactive sites. In consonance with Y6's results, the acceptor character is strongly related to EG, while the donor character has a stronger core participation (FREITAS et al., 2024). Regarding MEP, the observed alignment occurs exclusively between the negative MEP and f^- , further enhancing its donation capabilities. Another shortcoming for BZIC is its EG orientation that hinders its stacking (which influences the FF) due to its coexisting conformers (see Section 1.3.4). In summary, Y6 behaves like an acceptor with donation potential, while BZIC (an NFA), presents relevant donor features with acceptance potential at the end groups.

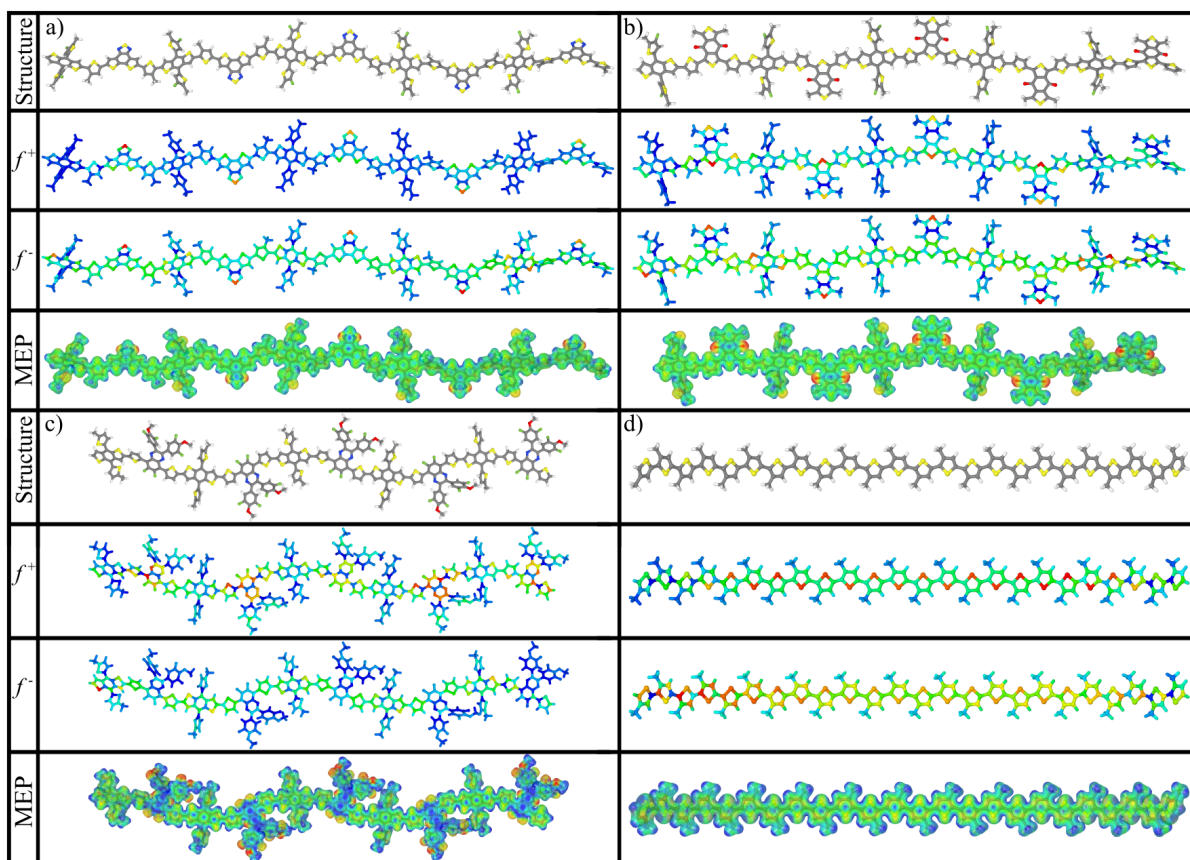
The fullerene acceptor, PCBM, showed similar results to Y6, in the sense that it also has stronger acceptor characteristics (f^+). All the relevant CAFI information is in PCBM's fullerene, and the side group is inert, despite presenting negative electrical potential. Both indexes present the same amount of highly reactive (red) sites. However, it is possible to say that f^+ shows an overall higher reactivity, given its other reactive sites (orange colored) that aren't present in f^- . Regarding MEP, there are pools of positive potential in over the cage, which enhances PCBM's acceptor character. A limiting factor for PCBM as an acceptor is its irregular stacking (WEI et al., 2020). In fact, a great and organized stacking could align f^+ and f^- reactive sites, facilitating carrier transport/transfer, which is not the case with typical fullerene-based devices. Despite its limitations, PCBM is employed in Y6/PM6 ternary organic solar cells as an additive, enhancing the PCE (GAO et al., 2020, p. 16; PAN et al., 2019; WEI et al., 2020; YU et al., 2019; YUAN et al., 2019).

Note that each acceptor has its particularities, however, Y6 is the one to present a strong acceptor character with relevant donor features, interesting MEP/CAFI alignment, and a stable conformation that allows for great stacking (DE PROFT et al., 2002; ZHANG et al., 2020; ZHU et al., 2020b) (enhancing FF and carrier transport and charge transfer). Moreover, the unexpected donor character of BZIC must be highlighted, demonstrating an undesired behavior for an NFA. Finally, PCBM's CAFI and MEP results underscore its electronic potential for ternary organic solar cell applications. Nevertheless, comprehensive studies are required to explore other relevant parameters.

1.3.8.2. DONORS' CAFI COMPARATIVE ANALYSIS

The donor polymers studied here were D18, PM6, both to pair up with Y6, HFQx-T and P3HT, to pair up with BZIC and PCBM, respectively. Herein, these studied polymers will be compared to each other at their saturated structures, to get a better understanding of the properties that make them good electron donors for OSC. Figure 1.43 brings the CAFI and MEP results of these saturated polymers, f^0 is omitted as only charge transfer related information is relevant for this discussion. As alternating or straightforward structures for polymers did not show relevant CAFI or MEP difference, only alternating structures are presented. The color scale is omitted, as each one has its own scale.

Figure 1.43. CAFE and MEP results for a)D18, b)PM6, c)HFQx-T and d)P3HT in their saturated conformation.



Source: Author.

The results obtained for D18 monomeric structure reveal a predominant donor character, as indicated by a higher number of highly reactive sites and overall greater reactivity regarding f^- . This suggests a higher probability of electron donation compared to its acceptance. Additionally, similar to Y6, the thiadiazole sulfur atom is identified as an amphiphilic site, which is significant for CT depending on the stacking configuration. In the saturated structure of D18, edge effects are observed on both sides, mainly for f^- , with consistent results at the central units. The overall reactivity is dominated by f^- , with the previously mentioned amphiphilic behavior on the structure (high reactivity on the same sites for f^+ and f^-). Regarding the MEP analysis, the thiadiazole potential is notable for exhibiting both positive and negative potential (with high reactivity values for f^+ and f^-), highlighting its relevance for CT. In general, these findings indicate that the material possesses ambivalent CT capabilities, similar to Y6.

The first notable PM6 result is the unusual acceptor character of its monomer (f^+), which exhibits a higher number of reactive sites, and donor features that are dominated by edge effects (f^-). This characteristic evidences its chemical similarity with Y6 and vanishes from the dimer stage onward (see Supplementary Material) so that the saturated structure reveals a stronger donor (f^-) character compared to the acceptor (f^+) one. Unlike D18, the donation and acceptance sites in PM6 do not correspond to each other. However, due to its complex structure and polymeric (branched) nature, it is plausible that these sites are sufficiently close in adjacent molecules into the device's active layer, allowing effective charge transfer/transport processes. The MEP indicates a negative electrical potential over the oxygen atoms, which are relatively close to regions with high f^- values. Conversely, there are no relevant positive electrical potentials close to sites with significant f^+ , indicating that PM6 might lack acceptance properties, compared to D18.

The monomeric structure of HFQx-T yields results similar to those of PM6, with a strong donor character (that is more pronounced in HFQx-T). Unlike PM6, this feature persists along the oligomer's saturation. Note that the donor character is concentrated on the leftmost side of the pentamer, mainly due to edge effects. Notice that the overall reactivity is higher for the f^+ index, which gives it a stronger acceptor than donor character, in relation to site accessibility. Finally, the intricate structure of HFQx-T indicates a possibly poor stacking and FF, as shown by experimental results (ZHOU et al., 2018). In particular, the positive potential observed on sites with high f^+ indexes, suggests an interaction between negatively charged acceptors centers of BZIC (at EG) and polymer accepting sites, hindering an effective CT (exciton dissociation) process. Together, these features provide the reasoning behind the poor PCE results in HFQx-T/BZIC-based OSCs (SHOAE et al., 2023).

Some edge effects are also noticed for saturated P3HT. Upon initial examination, f^+ seems more reactive due to the presence of red sites in the central region of the oligomeric system. However, edge effects concentrate these red sites on the leftmost side of P3HT. Despite this, there are still numerous (reactive) orange sites and an overall higher reactivity throughout the chain. In this sense, this material exhibits a stronger donor character with significant acceptance capabilities. The MEP spatial distribution further enhances the acceptance characteristics of the compound by aligning positive potential with high f^+ sites. The combination of these calculated properties indicates P3HT as a notable donor material with probable ambivalent charge transfer capability. Similar to its counterpart, P3HT's shortcomings are primarily related to structural issues, mainly related to its simplistic nature that hinders effective stacking.

Effective donor materials are expected to exhibit a dominant f^- index relative to f^+ . In this regard, D18, PM6, and P3HT successfully meet this criterion. Conversely, HFQx-T displayed the opposite behavior, showing a stronger acceptor character. Interestingly, its traditional counterpart in OSCs, BZIC, exhibits a slightly dominant donor character. This could explain the low PCE observed experimentally for these systems (FENG et al., 2017; WEI et al., 2020).

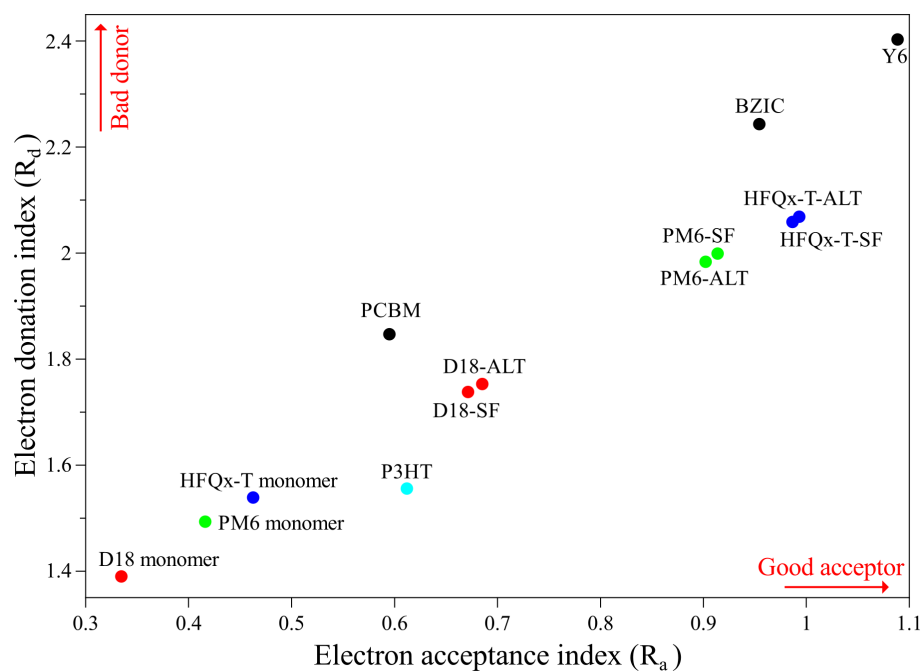
Especially in the case of polymer-based donors, beyond the local reactivity data, the MEP results bring important information regarding site alignment and molecular stacking/packing. Blue colors define sites with positive potential, while red regions present negative potential, so attractive (repulsive) electrostatic interactions are expected to occur between blue and red (red/red or blue/blue) sites. This feature indicates that effective molecular stacking must avoid face-to-face interaction which involves atoms with similar potentials, favoring the formation of slipped stacking.

In summary, this analysis highlights the key factors that made D18:Y6 a high-PCE OSC, while HFQx-T:BZIC showed poor performance. Structural studies at larger scales are necessary for better distinction between good and bad donors, once π - π interactions and molecular packing are extremely important, especially because of the alignment of reactive sites involved in CT processes. The CAFI results highlight the reactivity of a site, offering insights into a material's capacity to accept (f^+) and donate (f^-) electrons, along with details about site accessibility; specifically, whether energetically favorable acceptor (or donor) sites are accessible for electron acceptance (or withdrawal). To verify the overall donating and accepting capabilities, and conduct a truly comparative analysis regarding the distinct D and A materials, DAM and LEDAP analyses were conducted.

1.3.8.3. DONOR-ACCEPTOR MAP (DAM)

The comparative analysis on the global donation and acceptance capabilities of the studied materials were conducted by DAM, which is a graph of the electron donation index (R_d) vs the electron acceptance index (R_a) (see Appendix G for further details). Generally, low R_d index values are associated with good donors, while high R_a is associated with good acceptors (FREITAS et al., 2024; MARTÍNEZ et al., 2008). Figure 1.44 brings the DAM for all studied materials.

Figure 1.44. DAM obtained for donors (monomer and saturated oligomers) and acceptors.



Source: Author.

This map clarifies nuances that were difficult to pinpoint through the CAFI analysis. It shows that the SF and ALT structures have comparable R_d and R_a values, supporting earlier results. Moreover, the map highlights the distinction between the monomer and saturated structures, indicating that monomers have marginally better donation properties but worse acceptance features.

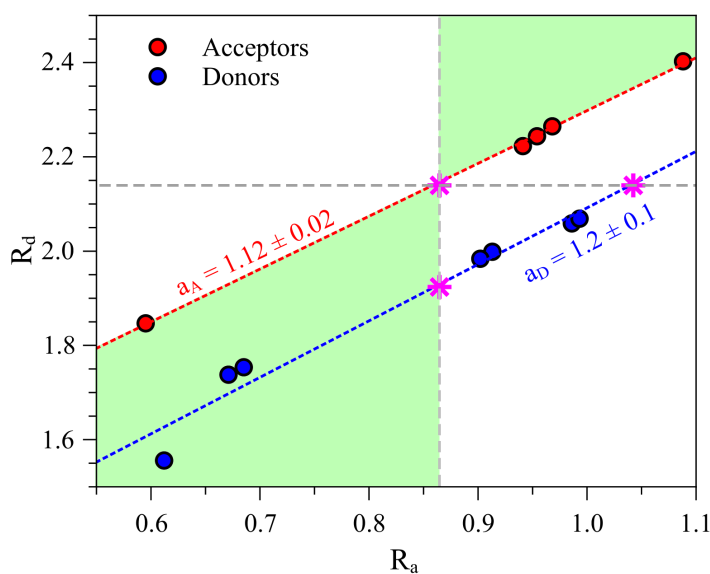
It is worth noting that D18 presents the best electron donation index among the NFA-based OSC donors, though worse than P3HT. Interestingly, the D18 acceptance index is better than PCBM's. Conversely, Y6 presents the highest indexes, making it the best acceptor and worst donor among all the structures.

The DAM analysis offers a new point of view on the CAFI result and the meaning of the reactivity in terms of acceptor and/or donor properties. As discussed before, the electron acceptance/donation capability can be summarized in terms of the f^+/f^- intensity and spatial distribution of reactive sites. However, it is still based on a qualitative analysis, which hinders the differentiation between similar materials, such as D18 and PM6. In this sense, the DAM provides a quantitative approach for comparing global donation and acceptance capabilities, allowing for the establishment of rankings. For instance, it indicates that D18 is a much better donor than PM6, which is not that far from HFQx-T. As far as the acceptor rankings, Y6 are

not so far from BZIC, though noticeably better, and both present almost doubled R_a than PCBM.

The analysis of Fig. 1.44 also shows interesting linear relationships. In particular, it's possible to fit straight lines for donors and acceptors, which have similar angular coefficients (almost parallel) but different linear coefficients. To illustrate and help this analysis, Figure 1.45 brings a simplified DAM, without the donor monomers, with some additional geometric information.

Figure 1.45. Linear behavior of A and D materials in DAM. The green zone defines zones of interest for lines linking promising D:A pairs (i.e. for $(R_d^A - R_d^D)/(R_a^A - R_a^D) > \frac{1}{2} (a_A + a_D)$).



Source: Author.

The observed almost parallel lines implies that the increase in acceptance capabilities of these materials is followed by a decrease in their donor properties at a constant rate ($a^* = \frac{1}{2} (a_A + a_D) \sim 1.16$). The definition of quasi-parallel linear behavior of $R_d(R_a)$ functions for D and A materials defines an interesting relation for efficient D:A systems, in such a way that the line linking the points $P^A(R_a^A, R_d^A)$ and $P^D(R_a^D, R_d^D)$ of DAM should present an angular coefficient given by $(R_d^A - R_d^D)/(R_a^A - R_a^D) > 1.16$ (green regions of Figure 1.45). Such a feature guarantees that D (A) material presents improved donor (acceptor) capacity concerning its A (D) counterpart (see the example magenta point shown in Fig. 1.45).

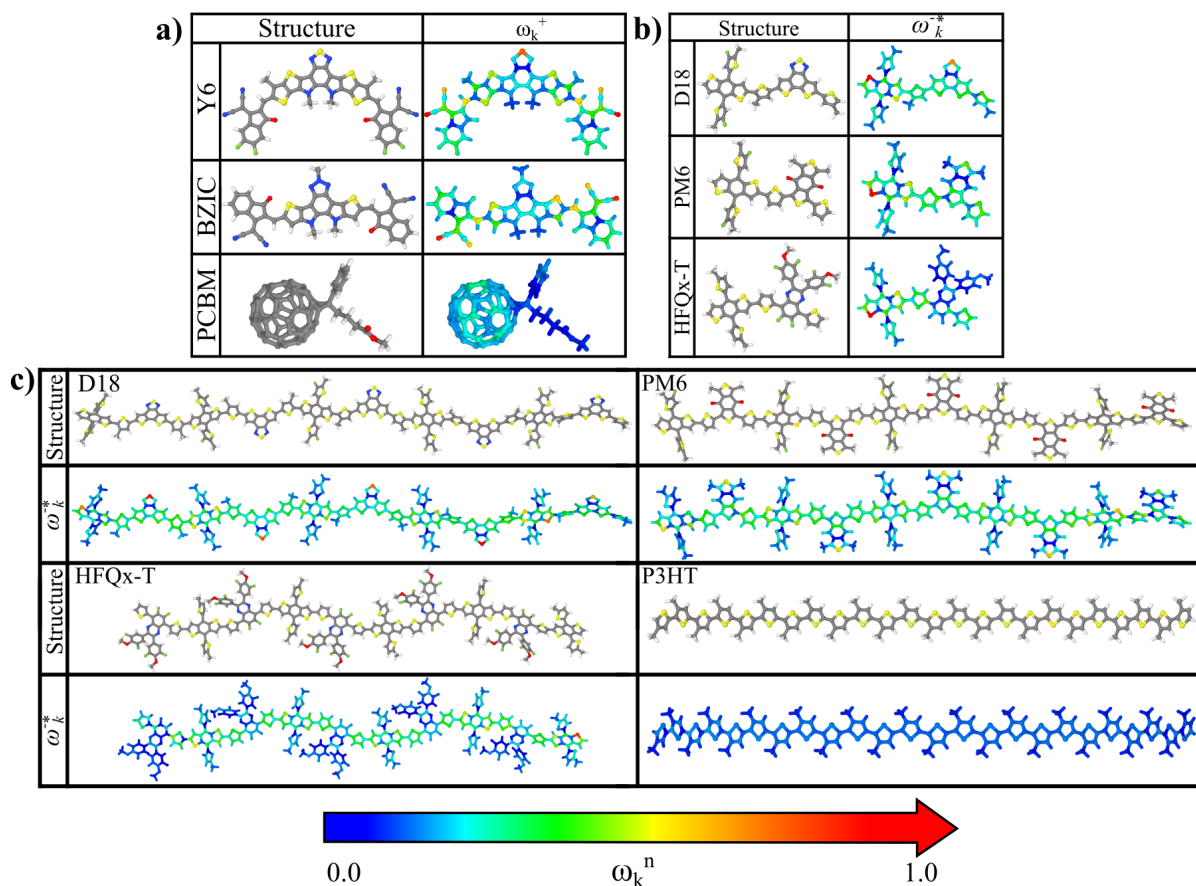
The CAFI+MEP results indicate the site's accessibility for electrons and holes, pointing towards a better molecular stacking for an acceptor-acceptor, donor/donor, and acceptor/donor pairs. On the other hand, DAM brings global information regarding

acceptor/donor capacities, that allows the comparison between distinct materials. The results presented here define the relevance of considering simple electronic descriptors to guide the choice and help the characterization of improved D:A pairs for OSC applications. From DAM we can trace an overall view of good acceptors and donors, mapping out R_a and R_d for each material. Moreover, by considering the limiting values $(R_d^A - R_d^D)/(R_a^A - R_a^D) > 1.16$ it is possible to identify promising D:A pairs from simple energetic data of the compounds, however, this assessment should be further refined by analyzing the relative alignment of their frontier orbital energy levels.

1.3.8.4. LOCAL ELECTRON DONATING AND ACCEPTING POWERS (LEDAP)

Aiming to bring the DAM's comparative features to the individual sites, as done for CAFI, LEDAP were evaluated. Figures 1.46.a-c bring the LEDAP results as color RGB scales. Red and blue represent high and low values of ω_k^+ , and ω_k^* . These values have been normalized to the maximum value of the distinct systems: a) acceptors, b) donor monomer, and c) donor-saturated oligomer (ALT structure). Additional conformations for BZIC, and SF saturated structures are presented in the Supplementary Material.

Figure 1.46. Local electron accepting (ω_k^+) and modified local electron donating (ω_k^{*-}) powers of a) acceptors, b) donor monomers, and c) donor oligomer ALT-structure. All the values were normalized to the highest value among the subgroups.



Source: Author.

Naturally, the highest LEDAP sites are the same as CAFI (see Eq. 1.9 and 1.10). Y6 (D18) defines a system with the highest electron accepting (donating) powers, and LEDAP values were used for normalization.

BZIC presents a slightly reduced LEDAP (compared to the CAFI scale), indicating that its electron accepting power is close to Y6. Conversely, PCBM does not present red sites, showing its reduced power compared to Y6 and BZIC.

Concerning donors, monomeric structures show similar electron donating powers for all three materials. For oligomers, it is evident the dominance of D18, followed by PM6 (with intermediate reactivity (orange sites) distributed along the main chain) and HFQx-T (with strong border effects). Lastly, there is a notably reduced electron donating power of P3HT compared to D18. All these results are consistent with those shown in Fig 1.44.

It is worth highlighting that the LEDAP analysis allows the local projection of DAM results, complementing the discussion and introducing a proper comparative pattern to

evaluate reactive/electron accepting(donating) sites. Based on these results the following ranking can be proposed: *i)* Donors - D18 >>PM6>HFQx-T>>P3HT; *ii)* Acceptors - Y6>BZIC>>PCBM, which are pretty compatible with experimental data (Wei et al., 2020).

In summary, LEDAP brings a local comparative analysis by combining general molecule's donation/acceptance capabilities to their CAFI, in such a way that rankings for electron accepting and donating capability were made. Moreover, combined with the previous CAFI results, it's possible to know from which sites the electrons are coming and going.

1.5. CONCLUSIONS OF THE CHAPTER

In this chapter, we've conducted electronic structure calculations and analyses for four sets of OSC active layer components: D18:Y6, PM6:Y6, HFQx-T:BZIC, and P3HT:PCBM. From these studies, it was possible to find some characteristics and properties that are desirable for good donor or acceptor materials. It was also possible to use CAFI as a means to understand the charge transfer process at the molecular scale and draw possible routes for charge transport in these systems. Moreover, as the same framework was applied to all materials, it was possible to compare them individually, by means of DAM and LEDAP analysis, and understand what makes D18:Y6 such an effective system for OSC.

Desirable characteristics and properties for effective donor and acceptor materials were identified and discussed. In particular, CAFI analysis was used to interpret CT processes at the molecular scale in these materials and to propose some of the most plausible pathways. The uniform framework applied to all materials enabled individual comparisons, elucidating why the D18 system is particularly effective for OSC.

It has also been shown the ambivalent CT properties of the Y6 acceptor. Notably, D18 and PM6 exhibit similar characteristics, with both showing significant site accessibility for electron donation and acceptance, although with better donation. Such amphiphilic behavior is indeed desirable to some extent to prevent charge-trapping effects.

The MEP results helped rationalize the poor PCE of the HFQx-T:BZIC pair. The positive electrostatic regions (blue) on HFQx-T force alignment to BZIC negative electrostatic regions (red). These blue regions are not donation regions (lack of f^- sites), thus the packing efficiency for the CT process is reduced.

Moreover, in this work, a method to analyze CAFI in a dimeric system was developed and applied to Y6's dimers found in its crystal structure: the charge transfer Fukui index (CTFI). This method shows significantly distinct results about simply applying CAFI in a

dimeric system and has a completely different result interpretation. Calculating CAFI directly in the dimeric system will show how both molecules would receive or donate electrons externally. On the other hand, CTFI shows how the components of the system exchange charges among themselves. Applying CTFI to Y6's dimers was essential to show that CAFI is indeed very useful as there is some agreement between both results, however, CTFI can better describe routes for charge transfer in Y6 in the context of its 3D interpenetrated crystal framework.

Additionally, the DAM study brought a quantitative approach to measure all selected materials' electron acceptance and donation capability. These results shone a light on a glaring issue of the low PCE studied D:A pairs: In the DAM, these compounds appeared vertically aligned, meaning they have a similar acceptance index (R_a). Conversely, known highly efficient pairs (D18:Y6 and PM6:Y6) appeared opposed to each other, presenting very distinct R_d and R_a . These observations led to the proposed relation for efficient D:A systems.

The LEDAP results offered a local approach to DAM. It is, in essence, the CAFI scaled by R_a and R_d , thus presenting the same sites for acceptance and donation, but allowing a comparative analysis. Combined with DAM, it was possible to rank the materials according to their capabilities: *i*) Donors - D18 >> PM6~HFQx-T >> P3HT; *ii*) Acceptors - Y6 > BZIC >> PCBM.

In general, the reactivity descriptor for CT process analysis was successful. CAFI revealed ambiphilic characteristics for the highest PCE pairs studied, and the site accessibility of each material. Aligned to MEP results, the high difference in PCE of the different pairs could be explored in the sense of packing and site alignment. Moreover, DAM and LEDAP offer quantitative results that further explain the different quality of the pairs. For the dimeric Y6 systems, the developed CTFI study showed with greater detail how charges go from one molecule to another, thus making it possible to understand charge routes in a crystal/stacked structure.

2 CHEMICAL ROUTES FROM 1-AZAFULVENALLENE TO PHENYLNITRENE

2.1. INTRODUCTION

The process of producing a specific chemical compound from another often involves multiple steps, with multiple short-lived intermediates that are difficult to study (and predict) once they cannot be observed under reaction conditions (MINISCI; HENDRICKSON; WENTRUP, 1976). In this context, computational studies could be of great use to provide a mechanistic rationale for the reaction's chemical pathway (KVASKOFF et al., 2014; MIRZAEI; WENTRUP, 2023).

Usually, the Intrinsic Reaction Coordinate (IRC) method (on Gaussian 16) is the tool used to search for different pathways and calculate their energy and the formation enthalpy. This tool is quite computationally expensive, for the molecules around 10 atoms (including H atoms), calculations can last about 2 hours (using 16 processors).

On the other hand, there are multiple computationally cheap descriptors that are basically inexpensive for a ~10-atom molecule. One of them is the reactivity descriptors, such as global and local softness (or hardness) and Fukui indexes, both extensively used in Chapter 1 and discussed in Appendixes D and E. The problem, however, is the calculated reactivity has the interpretation of being the reactivity towards a reactant, and in the case of a pathway, the subject is just evolving, without intermolecular interactions.

To apply the local descriptors to this context, first consider the local softness (LS). This is an atomic property that indicates the local relative polarizability of the electron cloud around the atoms. In the framework of the hard-soft acid-base (HSAB) principle, the comparative analysis of the LS allows us to identify which pair of atoms are prone to interact in a given chemical reaction (e.g. sites with similar LS values are supposed to react). In this context, we propose here using LS descriptors to interpret IRC results for model systems reported in the literature. A complementary tool is the Interaction Region Indicator (IRI), proposed by Lu T. and Chen Q. in 2021 (LU; CHEN, 2021), which reveals chemical bonds and weak interactions, offering information about steric effect, Van der Waals (VdW) interactions, and chemical bond unbalance which fills the gaps left by LS analysis, without adding relevant computational cost.

The possibility of using a cheap descriptor to find possible and probable chemical reaction pathways can be a valuable asset, as IRC requires previous knowledge of specific chemical directions to search for new paths. Therefore, knowing beforehand what the most probable atoms involved in the reaction would save time and resources in these studies.

This work is set to investigate the chemical pathways of 1-azafulvenallene from the usual IRC framework, and from the LS perspective, aiming to compare both results. In order to have as unbiased analysis as possible, this work was conducted in a collaborative way where one researcher (Prof. Didier Bégue - co-advisor of this thesis) ran IRC calculations as usually done, while the other (The author) ran LS and Interaction Region Indicator (IRI) calculations with no information on the model system, 1-azafulvenallene, but its structure. The LS result analysis was made first and then compared to IRC results. It was possible to show that LS' results are well aligned with IRC's in regard to which atoms interact to build the most likely pathway. It proves to be quite time and resource-saving to first look out for interactions with LS and then apply IRC calculations. Combined with information from IRI calculations, it was possible to propose two complete pathways from 1-Azafulvenallene to Phenylnitrene (the target molecule). Moreover, each IRC step could be used for LS and IRI calculations to further verify these alternative tools' potential.

The selected system is the pathway of the molecule 1-azafulvenallene towards phenylnitrene. These are reactive short-lived intermediary chemical species, usually achieved by flash vacuum pyrolysis (MIRZAEI; WENTRUP, 2023; POSADAS-HURTADO et al., 2025; WENTRUP, 2017; WIJERATNE et al., 2014). Finding a pathway to phenylnitrene and understanding possible byproducts are relevant given the variety of applications its derivatives have. For instance, aryl nitrenes are used in thermolysis and photolysis to obtain compounds such as amines, azepines, carbazoles and even for material functionalization (BAACHAOUI et al., 2021; POSADAS-HURTADO et al., 2025).

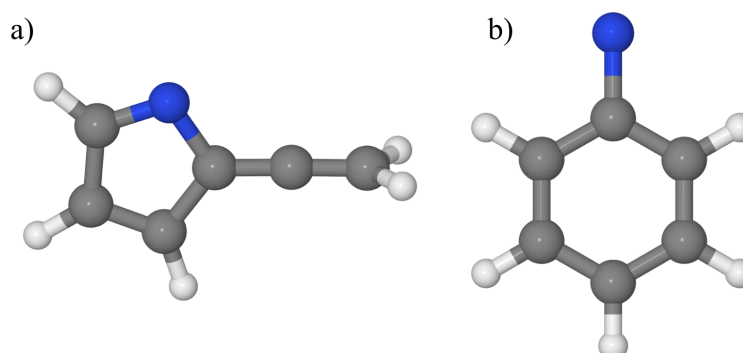
2.2. MATERIALS AND METHODOLOGY

In this section it is presented the selected molecules and the methods linked to LS estimation.

2.2.1. MATERIALS

The initial structure is the 1-azafulvenallene, and the targeted final structure is the phenylnitrene, both represented in 3D structures by Figure 2.1.

Figure 2.1. 3D structures of a) 1-azafulvenallene and b) phenylnitrene.



Source: Author

The idea is to go from a) to b) considering 2-atom interaction at each step. As the study progresses, new (intermediary) molecules are found (proposed), modeled and studied. All the molecules found will be presented in text as they are found. Double bonds are not represented in the figure.

2.2.2. METHODOLOGY

This work starts with two processes happening independently: *i*) 1-azafulvenallene is studied employing LS, finding interactions that lead to possible pathways to new structures, and *ii*) IRC calculations are done with 1-azafulvenallene, scanning new structures. These results can then be compared. Since LS only indicates atoms that are prone to interact, while IRC actually finds new structures, the steps towards phenylnitrene rely on the molecules resulting from the IRC.

In regards to LS, it's a property that measures the local chemical softness, *i.e.*, how much the electron cloud is changed when the total number of electrons changes. The more it changes, the softer it is. Mathematically it can be estimated as follows:

$$s_k^n = S f_k^n \quad (2.1)$$

$$S = \frac{1}{IP - EA} \quad (2.2)$$

$$IP = E(N - 1) - E(N) \quad (2.3)$$

$$EA = E(N) - E(N + 1) \quad (2.4)$$

where S is the global softness of the molecule, IP is the ionization potential and EA the electron affinity, E is the total energy and N is the total number of electrons. Notice that LS depends on S and on the CAFI value, calculated the same way as shown in Equations (1.3) to

(1.5). From Eq. (2.1) it's known that LS and CAFI are directly proportional, with S as a scaling factor.

Note that LS is a scaled variable allowing the evaluation of intermolecular interactions (between atoms of two different molecules). However, in this work, the interest relies on the intramolecular interaction between the atoms. Therefore, when comparing the LS of two atoms, the factor S plays no role, *i.e.*, it's the same thing if CAFI values were used.

The logic of using LS to evaluate interactions is to look for atoms with similar (high probability) and high (soft-soft interactions) s_k^{n1}/s_l^{n2} values. For two different molecules a threshold of 5% similarity has been used to define an effective intermolecular interaction (ALVES et al., 2020; MAIA; VENTORIM; BATAGIN-NETO, 2019), for the intramolecular interactions however, is a new area to be explored. To begin this work, the concern will be to consider the softest atoms to compare, not worrying much about the similarity.

This work is also set to investigate and give insights about the importance of different chemical softness characteristics and how other properties might interact with them to define intramolecular interactions that are likely to happen, building sort of an effective interaction descriptor. Some properties and relations used are softness similarity (Δs), sum of softness (Σs), and difference in atomic charges (ΔQ). Define as:

$$\Sigma s = s_i + s_j \quad (2.5)$$

$$\Delta s = |s_i - s_j| \quad (2.6)$$

$$\Delta Q = |Q_i - Q_j| \quad (2.7)$$

where s_i and s_j are the local softness for the two chosen atoms, and Q_i and Q_j are the Mulliken charge estimated for these atoms.

As mentioned, Δs has already been used in previous works to search for high-probability reactions, so its inclusion in a correlation equation seems logical (ALVES et al., 2020; MAIA; VENTORIM; BATAGIN-NETO, 2019). Another important variable for finding likely reactions is the effective chemical softness of the involved atom pairs, here, it is represented as Σs , which present high values for very soft pairs. Finally, intramolecular interactions are also supposed to be also driven by electrostatic effects (hard-hard interactions), thus ΔQ was included to describe this phenomenon. In short, a probable reaction should involve atoms with high s_k^n values (high Σs , *i.e.* soft atoms) with similar chemical softness (reduced Δs), and attractive (or small repulsive) electrostatic interactions (*i.e.* charges with distinct signals or reduced same net charges). Considering how the discussed magnitudes influence the likelihood of intramolecular interaction, they can be combined to build a

possible correlation between these values and the IRC calculated enthalpy (ΔH), which defines if a pathway is or is not possible. As a first approach, we have tried the following functional dependence of ΔH and the reactivity descriptors:

$$\Delta H \propto \frac{\Delta s}{\Delta Q \Sigma s} \quad (2.8)$$

Eq. 2.8 states that similar softness atoms are sought after among the softest ones. Moreover, charge difference might be preferential for attractive electrical forces, *i.e.*, for charges with different signs. For the same sign charges, ΔQ may be ignored. Notice that neither of the variables was supposed to present a nonlinear behavior (roots, logarithms, higher powers, etc), which might not be the case in reality.

Regarding how to obtain these properties, the framework used was DFT/B3LYP/6-311G(d,p), using Hirshfeld partitioning for LS (same as CAFI). The choice of the exchange-correlation function reflects previous studies from our group with small molecules, which have repeatedly shown that CAFI (and therefore LS) results in this framework are reliable (ALVES et al., 2020; COLEONE; BARBOZA; BATAGIN-NETO, 2021; CUBA et al., 2021; GALINDO et al., 2023; MAIA; VENTORIM; BATAGIN-NETO, 2019). The basis set of choice is a triple zeta Pople split valence set with (d,p) polarizable functions. Polarized triple zeta basis set was used to allow for greater flexibility to describe the atomic and molecular orbitals. Appendix B and C present more about exchange-correlation functionals and basis sets.

This chapter is a collaborative work with an ongoing project between Prof. Dr. Didier Bégué and Prof. Dr. Curt Wentrup (University of Queensland). The IRC calculations hereby were conducted by other members of the group. This method requires some configurations to be set, such as how many pathways should be searched, which atoms are involved in these reactions, the reaction direction (forward or reversed), and the step size (how much closer two atoms get between two SCF calculations, called a step).

For 1-azafulvenallene and each intermediary structure in the path towards phenylnitrene, different pathways were investigated based on chemical insights. Moreover, only forward direction was considered. Regarding step size, the default value of 1.0 Bohr ($\sim 0.53 \text{ \AA}$) was the choice. All IRC calculations were made considering the DFT/B3LYP/6-311G(d,p) framework, consistent with the LS approach.

To further explore details on atom-atom interactions, additional studies considering interaction region indicator (IRI) analyses were also conducted. Such an analysis requires

single point calculations on a neutral structure (calculated for LS) and is made with the aid of Multiwfn software (LU, 2024). IRI indicator is defined as (LU; CHEN, 2021):

$$IRI(\mathbf{r}) = \frac{|\nabla\rho(\mathbf{r})|}{[\rho(\mathbf{r})]^\alpha} \quad (2.9)$$

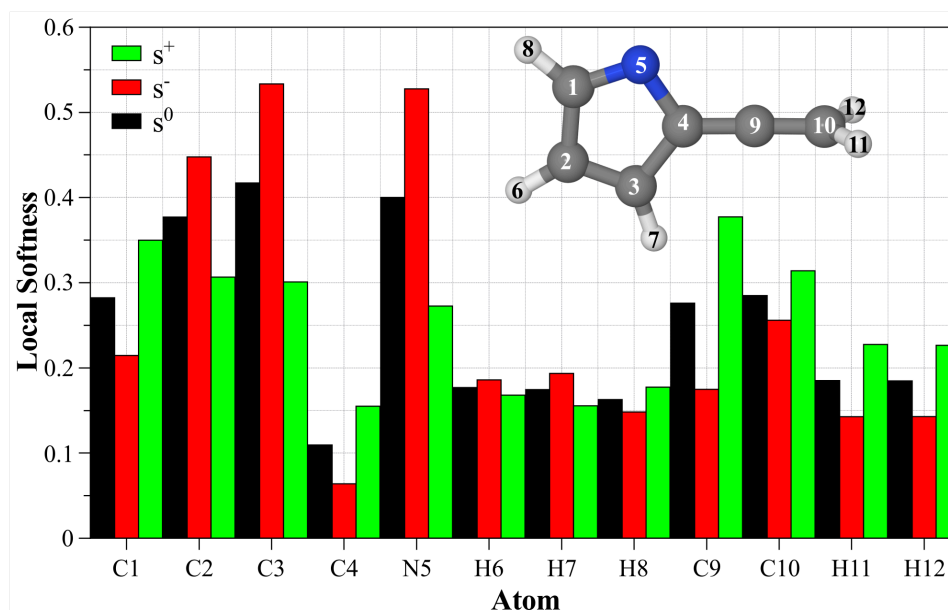
where α is an adjustable parameter set as 1.1. IRI is the gradient norm of electron density weighted by scaled electron density. Its result is presented as figures, isosurfaces of IRI that, depending on the isovalues (effective size), can show chemical bond, H bond, halogen bonds, steric effect, and VdW interactions. We consider this spatial descriptor defines a good complementary analysis tool to LS, helping to rationalize some results and offer new insights through the visualization of VdW interaction, chemical bond unbalance, and repulsion/steric effect. The previously mentioned DFT framework was also used for IRI.

2.3. RESULTS AND DISCUSSIONS

In this section will be presented and discussed our main results regarding LS/IRI and IRC study of 1-azafulvenallene and its derivatives. The subsections are related to each new molecule pointed by IRC/LS studies that was found by IRC, starting with 1-azafulvenallene and going to the next molecule(s) pointed by these results.

2.3.1. COMPARATIVE ANALYSIS BETWEEN IRC AND LS+IRI FOR 1-AZAFULVENALLENE

The 1-azafulvenallene is the starting point of the study. It was designed and optimized, followed by the LS and IRI calculations. The LS results are presented in Figure 2.2. and Table 2.1. The numbered structure is also presented to follow the discussions.

Figure 2.2. Numbered structure for 1-azafulvenallene and graph for local softness results.

Source: Author.

Table 2.1. Global (S), local softness (s^n), and atomic charge (Q) values for 1-azafulvenallene atoms.

S	3.0310	$\Delta E_T(\text{kcal/mol})$		0.0	ΔH	-	Atom	$Q(e)$
	s^+	s^-			s^0			
C9	0.3773	C3	0.5334	C3	0.4171	C1	0.0698	
C1	0.3499	N5	0.5276	N5	0.4001	C2	-0.1565	
C10	0.3140	C2	0.4477	C2	0.3771	C3	-0.0728	
C2	0.3066	C10	0.2559	C10	0.2849	C4	-0.1169	
C3	0.3009	C1	0.2146	C1	0.2823	N5	-0.2960	
N5	0.2726	H7	0.1935	C9	0.2760	H6	0.0985	
H11	0.2275	H6	0.1859	H11	0.1851	H7	0.0986	
H12	0.2265	C9	0.1748	H12	0.1847	H8	0.0944	
H8	0.1774	H8	0.1482	H6	0.1769	C9	0.1852	
H6	0.1680	H12	0.1428	H7	0.1745	C10	-0.1991	
H7	0.1555	H11	0.1427	H8	0.1628	H11	0.1476	
C4	0.1550	C4	0.0639	C4	0.1095	H12	0.1472	

Source: Author.

Similarly to CAFI, the interactions are supposed to occur between atoms with similar s^+/s^- (called here as charge transfer reaction, CTR) or s^0/s^0 (radical reaction, RR). The table is organized from the highest to lowest LS.

Starting from the CTR, notice that C9 is the softest atom for s^+ and C3 for s^- , making them the most likely atoms to react with each other. Other important combinations involving CTR are C9/N5, C9/C2, C1/C3, C1/N5 and C10/C3; N5; C2. However, the relative atomic distances must be also concerned in these reactions, so that even if two atoms present similar LS, they can be too far away from each other that all the structural changes needed to bond them would impose additional spatial restraints to the reaction. With that in mind, only combinations in which the atoms are separated by around (or less than) two bond typical lengths were considered. Combinations with already bonded atoms are also considered irrelevant once only the formation of new bonds are our initial focus.

In this sense, for CTR the considered combinations (in that order of relevance/probability to happen) are C9/C3, C9/N5 and C1/C3. For RR, C3/N5 build the most probable pair, followed by N5/C2. The latter also present interesting possibilities as CTR, even if less likely than the others.

Note that H11 and H12 present the highest positive charges, both bonded with C10. The atoms C10 and C9 show opposite charges at the same intensity. All the H atoms of the rings present similar positive charges, while the ring atoms' are all negative (except C1), with the most negative charge on N5. These results might help to identify relevant CTRs processes by considering the existence of additional attractive electrostatic effects.

To better summarize what was discussed and bring a quantitative view, Table 2.2 brings the aforementioned interaction and all of Eq. (2.8) variables. Δs and Σs are shown in absolute value, and ΔQ is calculated only if it involves charges of opposite signs.

Table 2.2. Compiled results for 1-azafulvenallene probable interactions.

Atoms	Int. Type	Δs	Σs	ΔQ	$\frac{\Delta s}{\Sigma s}$	$\frac{\Delta s}{\Delta Q * \Sigma s}$
C3/C9	s_3^-/s_9^+	0.1561	0.9106	0.2556	0.1761	0.6707
N5/C9	s_5^-/s_9^+	0.1504	0.9049	0.4813	0.1662	0.3453
C1/C3	s_1^-/s_3^+	0.1834	0.8833	0.1426	0.2076	1.4560
C3/N5	s_3^0/s_5^0	0.0170	0.8172	*	0.0208	*
C2/N5	s_2^+/s_5^-	0.2211	0.8342	*	0.2650	*
	s_2^-/s_5^+	0.1751	0.7202		0.2431	*

s_2^0/s_5^0	0.0230	0.7942	0.0290	*
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*atoms with same sign charges

Source: Author.

In terms of the general softness-based estimation, C3/N5 through RR should be the one of the most likely interactions to occur given the small Δs . However, considering Σs , the most probable interaction is C3/C9 via CTR, and this one even has relevant ΔQ to supposedly help the reaction. Notice that, comparatively, C3/N5's Δs is about 7 times smaller than C3/C9's, while the latter Σs is only about 1.1 times greater. However, it is important to highlight that, C3/N5 is an interaction happening between two atoms of the ring, while C3/C9 is not. With the ΔH result, the answer to which parameter is most important between Δs and Σs may arise. However, this observation about where the reaction takes place may be too problematic, to the point that it might not be possible to compare in-ring/in-ring to in-ring/out-ring atoms interactions.

Either way, the first results lead to a couple of possible reaction pathways. In the realm of CTR, C9/N5 appears as the most likely interaction to happen (according to the last 2 columns of Table 2.3), followed by C3/C9, which is a close option if ΔQ is not considered. This pair is actually good for comparing with the IRC calculated ΔH for the resulting interactions, since $\Delta s_{5/9} < \Delta s_{3/9}$ (*i.e.* better) while $\Sigma s_{5/9} < \Sigma s_{3/9}$ (*i.e.* worst) so it might be possible to better understand which is the most relevant set of parameters.

Lastly, considering RR, the most probable reactions involve C3/N5 and C2/N5 pairs (in this order). Both reactions take place into the ring and show very small $\Delta s/\Sigma s$ compared to reactions with out-ring molecules. This is one interaction in which the descriptors are insufficient, as the reduction of the ring size (from five to four atoms) should be unfavorable, and LS results pointed them as favorable reactions. This limitation is clearly associated with the absence of molecular geometric features into the descriptors.

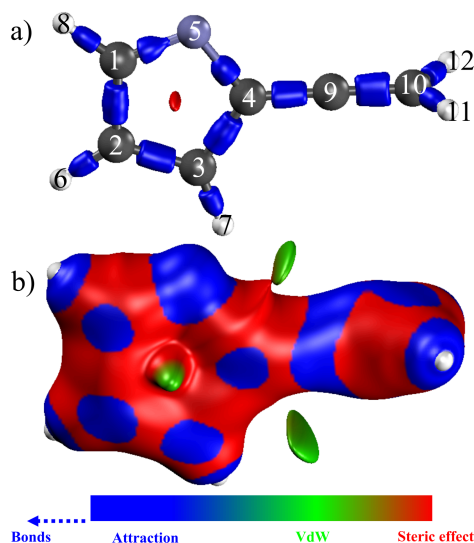
Summarizing:

- C9/N5 (and C9/C3) defines a relevant CTR where atom C9 bonds to N5 (C3) by forming a triangular bond: C4-N5-C9 (C4-C3-C9). This process can lead to C4-N5 (C3-C4) bond break, leading to a six-atom ring. Another possibility involves C9-C4 bond breaking, keeping C9/N5 (C9/C3) connection;
- C3/N5 (C2/N5) is a RR the atoms are supposed to approach one each other, breaking the weakest bond to C4 (C1) with the formation of a high energy four-ring atom;

All these interactions can indeed lead to bonds-breaking and additional structural changes that can not be directly predicted by simple LS descriptors.

To account for LS weaknesses, the IRI analysis is used, Figure 2.3 brings IRI results considering an isovalue of *a)* 0.9, and *b)* 2.5. Multiple regions with different types of interactions are presented.

Figure 2.3. 1-azafulvenallene's IRI result considering isovalue of *a)* 0.9, and *b)* 2.5.

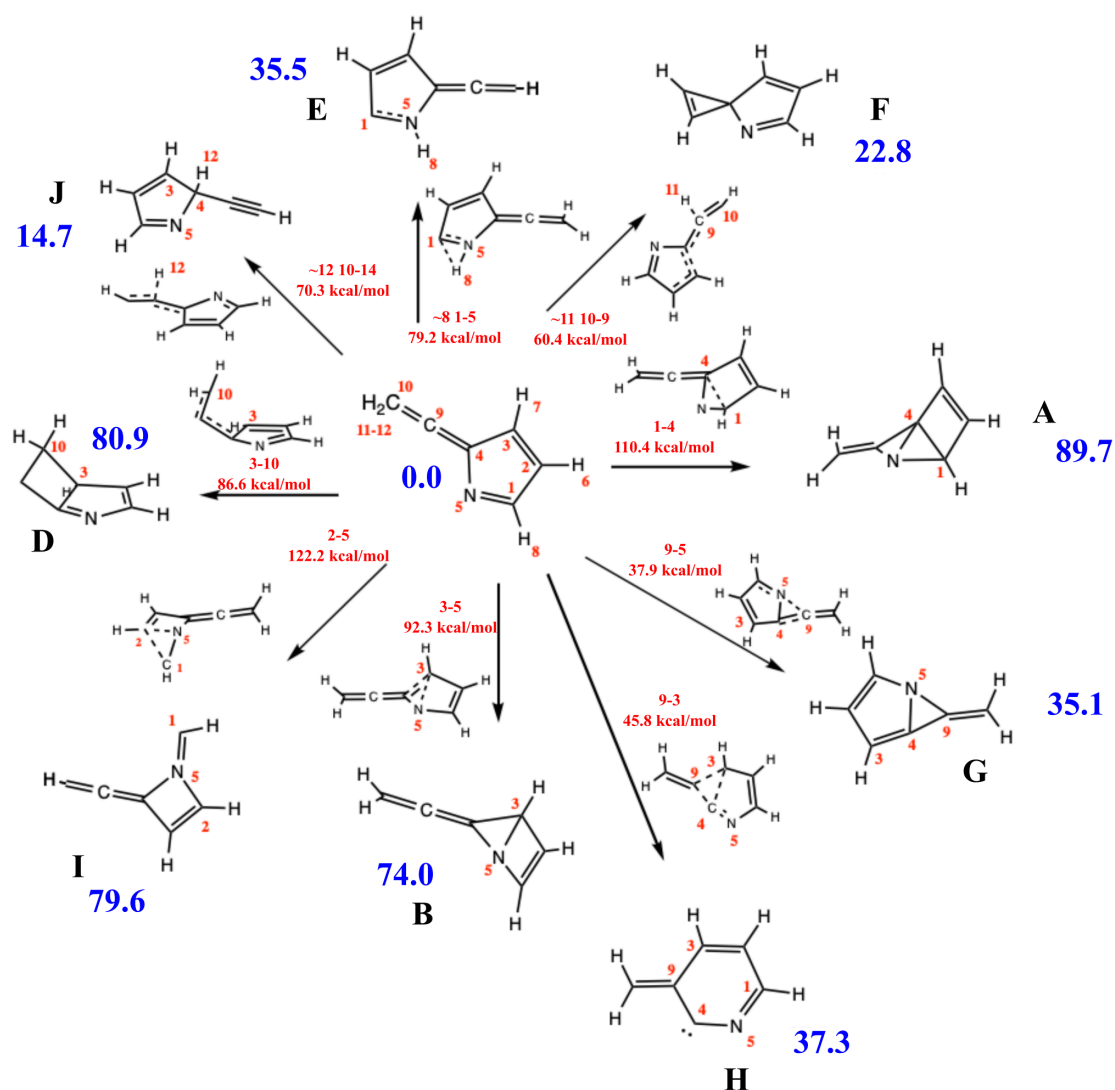


Source: Author.

From Fig2.3a it is possible to notice two important features, first is the bond imbalance on N5, C4-N5 has a different shape than C1-N5, which extends a little bit more towards N5. The last is the red region in the middle of the ring, representing a steric effect, indicating that in-ring interactions (s_1^-/s_3^+ , s_3^0/s_5^0 , s_2^{n1}/s_9^{n2}) have a bigger barrier to face. On the other hand, b) results help choosing a path between C9-N5 or C9-C3. The first presents a slight repulsion bulge around the C4-N5 bond, and a smaller VdW effect than the one between C9-C3. Remember that does not necessarily mean a smaller enthalpy, regarding the proposed correlation interaction with N would be less energetic. Most importantly, IRI results are well related to LS results, supporting LS with important insight on bonds and repulsive interactions.

In a more usual sense, the prediction of specific reaction pathways can be done via IRC, by choosing and investigating specific interactions. Figure 2.4 displays possible routes identified via IRC. The nine resulting new paths and structures were named as paths A to I, and the structures as Aza-X (where X=A, B, ... I). Their total energy variation concerning 1-azafulvenallene (ΔE_T , in blue) and enthalpy of formation (ΔH , in red) are also shown (both in kcal/mol). A summarized version of these results is presented in Table 2.4.

Figure 2.4. IRC results for 1-azafulvenallene, showing new paths (A to I) and their ΔE_T and ΔH , in kcal/mol.



Source: D. Bégué, personal communication, 2023.

Table 2.3. Summarized 1-azafulvenallene IRC results.

Pathway	Interaction	ΔH	ΔE_T
A	1-4	110.4	89.7
B	3-5	92.3	74.0
C	1-3	unfavorable	
D	3-10	86.6	80.9
E	~8 1-5	79.2	35.5
F	~11 10-9	60.4	22.8
G	9-5	37.9	35.5
H	9-3	45.5	37.3

I	2-5	122.2	79.6
J	~12 10-4	70.3	14.7

Source: Author.

From Figure 2.3 and Table 2.4, it can be seen paths G (N5-C9) and H (C3-C9) possess the lowest ΔH by a large margin, indicating their relevance in relation to the other paths (which aren't eligible for further investigation). This result is quite interesting as these paths are the ones found as most likely ones by the LS study.

Regarding our overall descriptor ΔH , we see that path G has $\Delta H_G=37.9$ kcal/mol, while H has $\Delta H_H=45.5$ kcal/mol, a ratio (G/H) of 0.83. On the other hand, LS results pointed out G as the best pathway (although worst Σs than H) and the ratio G/H considering $\Delta s/\Sigma s$ was 0.94, and 0.51 when considering $\Delta s/(\Delta Q\Sigma s)$. This indicates that ΔQ might not be that relevant for a correlation equation, while $\Delta s/\Sigma s$ was already pretty close. Moreover, it seems that Δs might pose a stronger influence in the correlation than Σs .

Still on the note, the RR interactions found by LS were also identified by IRC as paths B and I, leading to relevant insights. The combinations for B and I had very low $\Delta s/\Sigma s$ (LS result) but one of the highest ΔH (IRC results), such a divergence can be clearly explained by IRI results where it's possible to see relevant repulsion in the center of the ring, which increases the cost for all in-ring interaction (A, B, C, and I). However, IRI does not offer a direct numerical approach that could be incorporated in the correlation equation.

Path D was not investigated by LS by choice. The interaction C3-C10 is indeed somewhat relevant in terms of Δs and Σs , however these atoms are quite far from each other. Distance is not necessarily an impediment for interaction, but such an interaction would require severe structural changes, which might lead to different intermediary LS results.

Finally, paths E, F, and J show interactions that were not identified by LS, where hydrogen moves to a new position. The notation is $\sim X Y-Z$, which means the H atom X moved from atom Y to Z. In general, the H atoms are hard atoms (with low softness), thus disregarded as possible soft-soft interaction, being more likely associated with hard-hard (electrostatic) ones. Among these paths, F has the best ΔH , the third lowest overall (losing to paths G and H). Therefore, a relevant result from the IRC perspective.

Given the above presented considerations, LS analysis defines an interesting tool to guide IRC and help its interpretation, allowing to identify some of the most likely (less energetic) pathways from 1-azafulvenallene. In fact it is surprising that such simple

descriptors (and other related ones, as described in Eq. (2.8)) can provide enough data to distinguish between probable chemical pathways.

Moreover, important shortcomings in LS analysis were also found. Firstly, LS will only point to the very best possibilities, as it clearly did for paths G and H. Secondly, LS analysis does not consider the structure, meaning in-ring interactions and distant atoms interaction could be regarded as great options (in-ring can be “solved” by IRI analysis). Thirdly, LS will not consider H atom interactions, as these are the hardest atoms in the molecule. Finally, this first set of results points towards Δs being impactful for the overall descriptor, ΔH , however both atoms still need to be as soft as possible, meaning Σs is of vital importance.

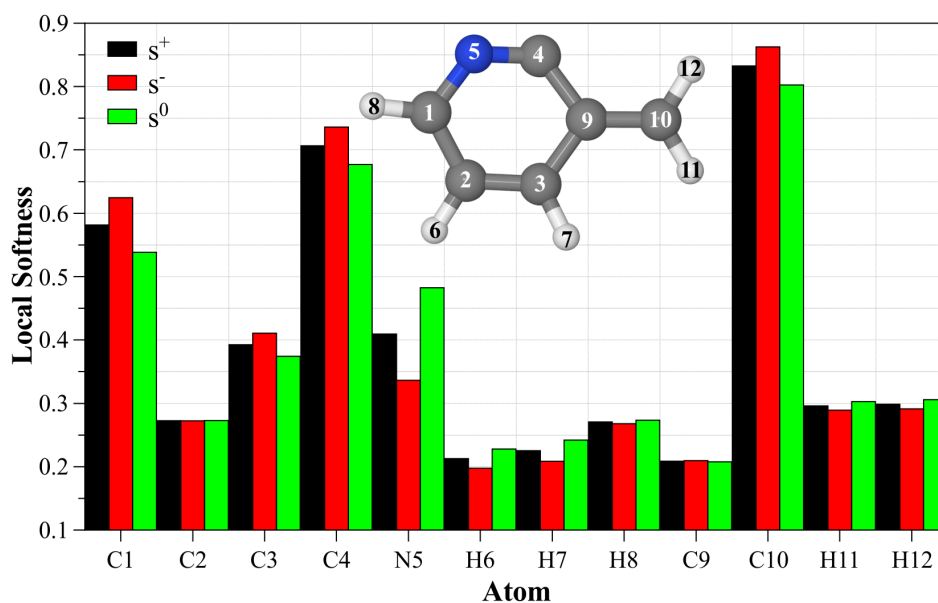
The best-found chemical paths G and H were considered in the subsequent studies. Note that these structures have been obtained from IRC results. LS analysis only allows the identification of atom pairs that are going to interact, but not the resulting structures coming from these interactions.

2.3.2. COMPLETE PATHWAY FROM LS AND IRI ANALYSIS

Considering finding a whole path through LS and IRI analysis (but using IRC found structures) the considered resulting structure from 1-azafulvenallen was Aza-H. From LS analysis alone, Aza-G had a slight advantage over Aza-H, however, the IRI results went in favor of Aza-H.

2.3.2.1. AZA-H

The results presented for 1-azafulvenallene IRI and LS results pointed to C3-C9 interaction as being a great candidate for finding a pathway to phenylnitrene. This interaction resulted in the Aza-H structure, which IRI and LS analysis is presented here. The structure used for the calculations was obtained from IRC results, which actually pointed to a closed and open-shell structures (CS and OS, respectively). Figure 2.5 and Table 2.4 bring the results obtained for the CS structure (atomic charges included).

Figure 2.5. Numbered structure for Aza-H (CS) and graph for local softness results.

Source: Author.

Table 2.4. ΔH , ΔE_T , S , LS and Q values for Aza-H (CS) atoms.

S	4.7068	$\Delta E_T(\text{kcal/mol})$	37.7	ΔH	45.8		
	s^+	s^-	s^0			Atom	Q
C10	0.8026	C10	0.8626	C10	0.8326	C1	0.0340
C4	0.6770	C4	0.7361	C4	0.7066	C2	-0.1840
C1	0.5384	C1	0.6246	C1	0.5815	C3	-0.0227
N5	0.4824	C2	0.4107	C3	0.4094	C4	0.1263
C3	0.3743	C3	0.3364	C2	0.3925	N5	-0.2064
H12	0.3058	C9	0.2913	C9	0.2985	H6	0.1107
H11	0.3027	H11	0.2892	N5	0.2959	H7	0.1141
H8	0.2734	H12	0.2724	H12	0.2726	H8	0.1287
C2	0.2728	H8	0.2679	H11	0.2706	C9	-0.1515
H7	0.2420	H6	0.2096	H8	0.2253	C10	-0.1717
H6	0.2279	H7	0.2085	H7	0.2127	H11	0.1090
C9	0.2077	N5	0.1976	H6	0.2086	H12	0.1134

Source: Author.

C4 and C10 stand out as the softest atoms considering all the indexes. Therefore C4/C10 is clearly the most likely interaction. A secondary interaction comes from C1/C4 coupling, also for every combination (CTR and RR). It could be argued that C1/C10 is also a

likely interaction, as C1 is the third atom in relation to LS, but it can be disregarded given the long interatomic C1-C10 distance. On a similar note, C3-C10 is also somewhat relevant, but C3 is much harder than its peers. Table 2.5 presents the compiled results and calculations of other descriptors.

Table 2.5. Compiled results for Aza-H (CS) probable interactions.

Atoms	Int. Type	Δs	Σs	ΔQ	$\frac{\Delta s}{\Sigma s}$	$\frac{\Delta s}{\Delta Q * \Sigma s}$
C4/C10	s_4^+/s_{10}^-	0.1856	1.5396	0.2980	0.1206	0.4047
	s_4^-/s_{10}^+	0.0665	1.5387		0.0432	0.1450
	s_4^0/s_{10}^0	0.1260	1.5391		0.0819	0.2748
C1/C4	s_1^+/s_4^-	0.1360	0.8536	*	0.1551	*
	s_1^-/s_4^+	0.0587	0.7283		0.0806	*
	s_1^0/s_4^0	0.0386	0.7909		0.0971	*

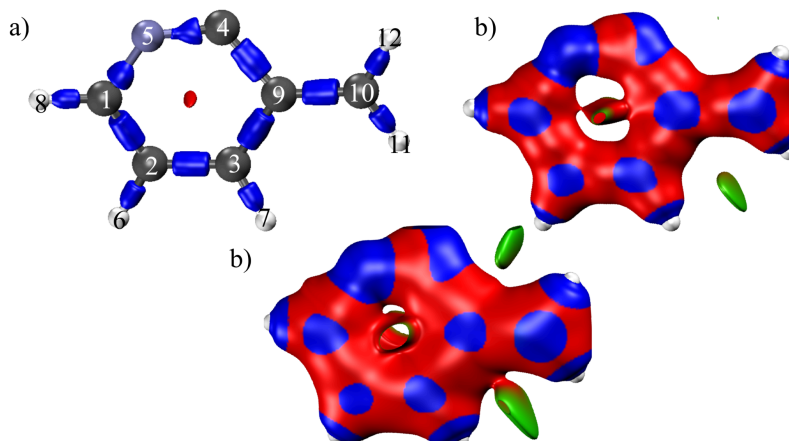
*atoms with same sign charges

Source: Author.

Regarding the resulting structures of these interactions, C4/10 may result in a seven-ring molecule or a transitional structure where C4, C10, and C9 build a cyclic three-atom bond. Finally, C1/C4 shows a pathway where the five-atom ring is recovered, but with the N atom out of it. Notice that, from previous studies, in-ring/in-ring interactions were overestimated because they led a five- to a four-atom ring, an unfavorable interaction. However, Aza-H has a bigger ring structure that might withstand such an effect. In summary, C4/C10 is more likely to happen (demanding less energy), but C1/C4 might also be relevant.

To bring a different point of view, Figure 2.6 shows IRI results for Aza-H (CS) for three different isovalues. It employs the same color definitions as Fig. 2.3.

Figure 2.6. Aza-H (CS)'s IRI result considering isovalue of a) 0.9, b) 2.1 and c) 2.5.



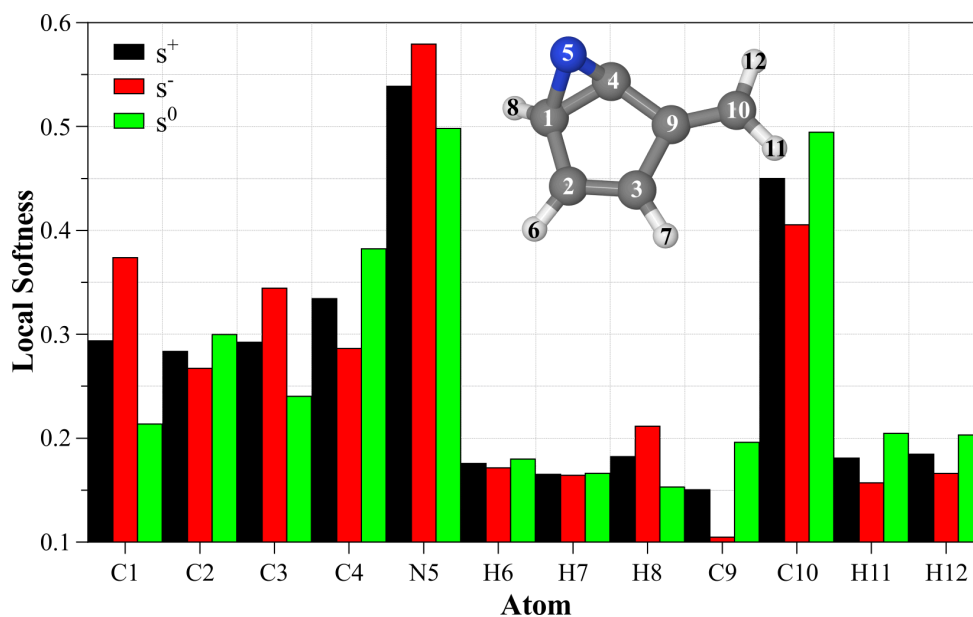
Source: Author.

Once again, Fig. 2.6.a shows asymmetry on N5's bonds, here C4-N5 seems to have a slightly better interaction than C1-N5. Moreover, it shows a steric effect which can cause difficult in-ring interactions that cross the ring (for instance, C2-C4, C3-N5, etc). However, as confirmed on b) and c), some in-ring atoms are still feasible, such as C1-C4, given the gap of repulsive surface in the middle of the ring (noticed even for high isosurface values). Figure 2.6.b shows a much greater VdW interaction in the path between C3 and C10 than between C4-C10 (barely visible on b), but clear on c) with a bigger isosurface).

In conclusion, IRI clarifies C1-C4 as a possible path, as well as showing a new path in C3-C10 (which is actually relevant for the OS structure - see Appendix J). In addition to LS results, there are 3 possible pathways: C1-C4, leading to Aza-L (five atom ring, with C1-N5-C4-C1 cycle), C4-C10, leading to Aza-O (five atom ring, with C9-C10-C3-C9 cycle), and C3-C10, leading to Aza-W4 (seven atom ring structure). As this section's main path, Aza-L was chosen as the next step as it has the lowest $\Delta s/\Sigma s$ value and IRI confirms this in-ring interaction is feasible.

2.3.2.2 AZA-L

The structure named Aza-L was obtained from IRC calculation through the interaction of C1 and C4 atoms. It's the second step from 1-azafulvenallene to phenylnitrene. Figure 2.7 and Table 2.6 shows the results for LS analysis (atomic charges included).

Figure 2.7. Numbered structure for Aza-L and graph for local softness results.**Table 2.6.** ΔH , ΔE_T , S , LS and Q values for Aza-L atoms.

S	3.2314	$\Delta E_T(\text{kcal/mol})$	43.5	ΔH	22.0	Atom	Q
	s^+	s^-		s^0			
N5	0.4982	N5 0.5793	N5	0.5387		C4	0.0496
C10	0.4945	C10 0.4054	C10	0.4499		C1	-0.1280
C4	0.3823	C1 0.3738	C4	0.3343		N5	-0.1788
C2	0.2998	C3 0.3444	C1	0.2937		H8	0.1318
C3	0.2403	C4 0.2863	C3	0.2923		C2	-0.0475
C1	0.2136	C2 0.2672	C2	0.2835		H6	0.1064
H11	0.2046	H8 0.211	H12	0.1846		C3	-0.1274
H12	0.2031	H6 0.1714	H8	0.1822		H7	0.1050
C9	0.1960	H12 0.1661	H11	0.1808		C9	-0.0231
H6	0.1799	H7 0.1642	H6	0.1757		C10	-0.1269
H7	0.1662	H11 0.1570	H7	0.1652		H11	0.1240
H8	0.1530	C9 0.1047	C9	0.1504		H12	0.1149

Source: Author.

It is possible to see a clear dominance of N5 as presenting the highest LS values, followed by C10, for all the indexes. They are followed by C4 (in relation to s^+ and s^0) and C1

(for s^-). A great distance separates C10 from N5, which prevents interactions between them. In fact, given N5's spatial positioning, the atoms that could physically interact with it are C2 and C9. The first interaction might be indeed possible, while the latter is the hardest atom of the molecule. On another note, a captivating interaction is C4/C10, which might lead to a six-atom ring again. Although C1-N5 bond breaking is expected to be found, no relevant information can be gathered with LS study.

Table 2.7 brings the compiled results as well as $\Delta s/\Sigma s$ and Eq. (2.8) parameters.

Table 2.7. Compiled results for Aza-L probable interactions.

Atoms	Int. Type	Δs	Σs	ΔQ	$\frac{\Delta s}{\Sigma s}$	$\frac{\Delta s}{\Delta Q * \Sigma s}$
C4/C10	s_4^+/s_{10}^-	0.0231	0.7877	0.1765	0.0293	0.1661
	s_4^0/s_{10}^0	0.1156	0.7843		0.1474	0.8351
C3/C10	s_3^-/s_{10}^+	0.1501	0.8389	*	0.1789	*
N5/C2	s_5^-/s_2^+	0.2795	0.8791	*	0.3179	*

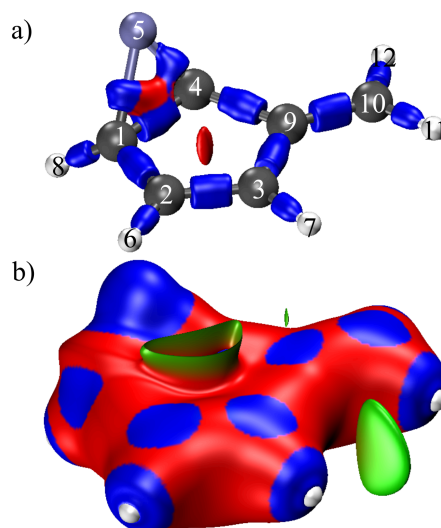
*atoms with same sign charges

Source: Author.

It is clear that C4/C10 is the most likely interaction, especially considering s_4^+/s_{10}^- , which is considerably low considering all previous results. On the other hand, N3/C5 has its $\Delta s/\Sigma s$ on the higher end. In short, this set of results could not predict the bond breaking, which is expected as it's not the focus of LS analysis. Moreover, it showed yet another result pointing towards growing the ring.

For this structure, IRI is specially relevant, since it's clear that LS analysis will not predict bond breaking, at best it can show that a bond is somewhat unstable if between a hard and a soft atom. Figure 2.8 brings these results considering two isosurface values.

Figure 2.8. Aza-L's IRI result considering isovalue of a) 0.9, and b) 2.5.



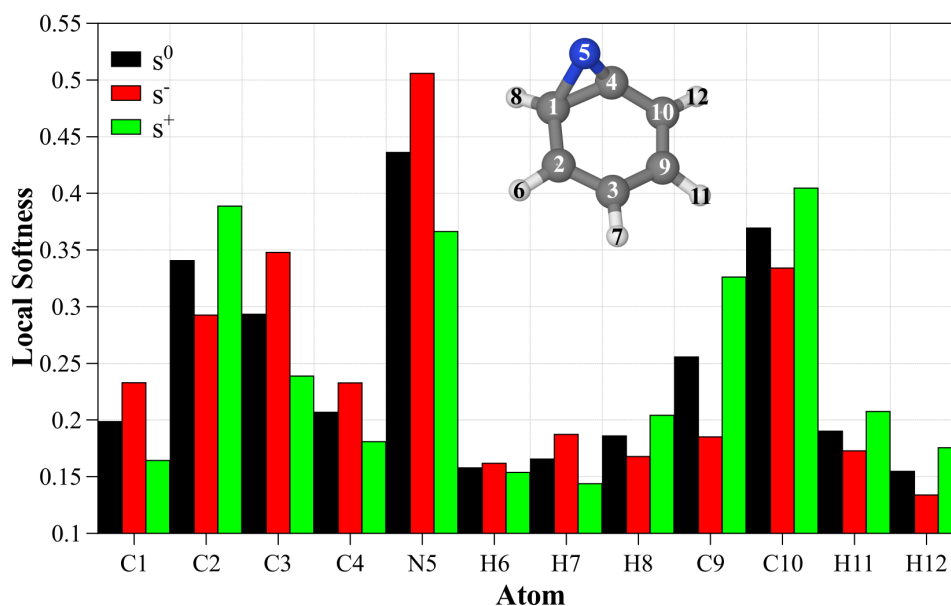
Source: Author.

The main interest with these results is to find some indication of bond-breaking, as it is impossible for LS to give such information. In that regard, on (a) there is a clear unbalance in bonds at C1-N5-C4-C2, where C1-C5 has less attractive interactions and more repulsive interactions. Moreover, (b) reinforces that behavior showing a repulsive bulge between C1 and N5, indicating that a bond breaking could occur. Another observation is VdW interaction between C3-C10, indicating their interaction (already pointed by LS results). The interaction C4-C10 has a much less relevant VdW interaction, however a more interesting LS result. Lastly, regarding a possible C2-N5, there is indeed another VdW surface that might be indicating this interaction.

In summary, LS+IRI analysis on Aza-L indicates three clear possibilities: *i*) C1-N5 bond breaking, leading to Aza-N; *ii*) C3 and C10 interaction, leading to a structure similar to Aza-P, and *iii*) C4 and C10 interaction, leading to Aza-P itself. For this section pathway, let's continue the analysis with Aza-P, given two out of three pathways lead to it, and it presented a very low $\Delta s/\Sigma s$ (considering C4-C10).

2.3.2.3. AZA-P

The structure for Aza-P was obtained through IRC calculations by interacting atoms C4 and C10. It's the third step towards phenylnitrene. Figure 2.9 and Table 2.8 brings the results for its LS analysis (atomic charges included).

Figure 2.9. Numbered structure for Aza-P and graph for local softness results.

Source: Author.

Table 2.8. ΔH , ΔE_T , S , LS and Q values for Aza-P atoms.

S	2.9545	$\Delta E_T(\text{kcal/mol})$		*	$\Delta H = *$	Atom	Q
	S^+	S^-			S^0		
C10	0.4046	N5	0.5058	N5	0.4361	C1	-0.1148
C2	0.3887	C3	0.3479	C10	0.3694	C2	-0.0642
N5	0.3663	C10	0.3341	C2	0.3406	C3	-0.1003
C9	0.3261	C2	0.2925	C3	0.2933	C4	0.0841
C3	0.2388	C1	0.2329	C9	0.2556	N5	-0.1945
H11	0.2075	C4	0.2327	C4	0.2068	H6	0.1024
H8	0.2042	H7	0.1873	C1	0.1986	H7	0.1241
C4	0.1809	C9	0.1851	H11	0.1902	H8	0.1067
H12	0.1755	H11	0.1728	H8	0.1860	C9	-0.1154
C1	0.1643	H8	0.1678	H7	0.1655	C10	-0.0643
H6	0.1538	H6	0.1618	H6	0.1578	H11	0.1220
H7	0.1438	H12	0.1339	H12	0.1547	H12	0.1141

* data not available

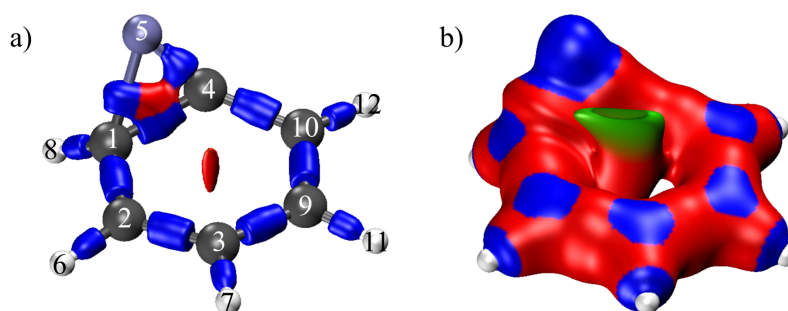
Source: Author.

Before talking about the LS result itself, it's important to highlight that Aza-P is on bond break (C1-N5) from phenylnitrene, which is unlikely to be observed from these results.

Regarding the LS, the dominance of N5 and C10 noticed for Aza-L is still present here, however C2 and C3 are also among the softest atoms. Naturally, N5-C10 is the first interaction to be highlighted given the high softness of both atoms, and unlike on Aza-L, these atoms are not too far apart. On the other hand, N5 is still bonded to C1, which won't allow its interaction properly. The C1 atom is particularly hard (lowest s^+ among the C), while N5 is the softest atom overall, which could indicate an unstable bond.

As C3 shows itself softer, its interaction with C10 turns out to be relevant. This bonding would likely return Aza-P to something similar to Aza-L. Other interactions rely on N5, namely C2-N5 and C3-N5. Somewhat similar to what was noticed for Aza-L. However, neither interaction brings the molecule closer to phenylnitrene. To observe if there's a chance of Aza-P going to phenylnitrene, IRI analysis is essential. Figure 2.10 brings the IRI results.

Figure 2.10. Aza-P's IRI result considering isovalue of a) 0.9, and b) 2.1.



Source: Author.

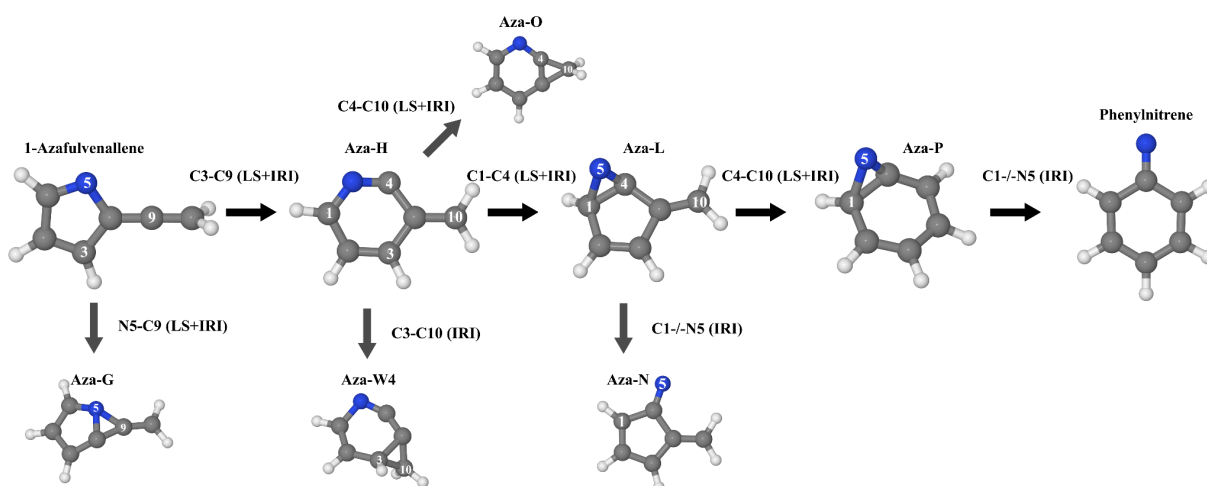
It's noticeable how similar this result is to Aza-L's. On (a) there's chemical bond unbalance, favoring C4-N5 bond over C1-N5, with repulsion interaction close to C1. Still similar to Aza-L, (b) shows a repulsion bulge between C1 and N5. All indicatives on bond breaking. As this is a six-atom ring molecule, there is a gap of repulsion surface around the region of atoms C3, C9, and C10, possibly allowing the aforementioned C3-C10 interaction (return to something similar to Aza-L). This is indeed a possibility, and calculating its energetic cost is important to give a quantitative analysis to the study, the reason why IRC studies are important.

In conclusion, IRI results made it possible to find the path from Aza-P to phenylnitrene by breaking the C1-N5 bond. It also supports one of the few possible interactions identified by LS studies, the C3-C10 interaction. With that, a path from 1-azafulvenallene to phenylnitrene is completed.

2.3.2.4. PATHWAY SUMMARY AND OUTLOOK

With the use of LS and IRI studies, it was possible to find a complete pathway from 1-azafulvenallene to phenylnitrene by identifying possible new bonds or even bond breaking. The final pathway was: 1-azafulvenallene $\rightarrow$ Aza-H $\rightarrow$ Aza-L $\rightarrow$ Aza-P $\rightarrow$ Phenylnitrene. Notice that at each step there were other options to follow, making for five alternative routes. Figure 2.11 brings the summary of the found pathway and the alternative routes. X-Y represents the bond between the atoms X and Y, while X-/Y represents the bond breaking between them, also (LS+IRI), (IRI), shows which methods allowed for finding such interaction.

Figure 2.11. Summary of 1-azafulvenallene path to phenylnitrene using LS and IRI approach.



Source: Author.

The “direct” route, highlighted by the black arrows, is the one presented along Section 2.3.2. There are at least four alternative paths to be investigated. In the next few sections they will be discussed, starting with the ones closest to the goal, phenylnitrene.

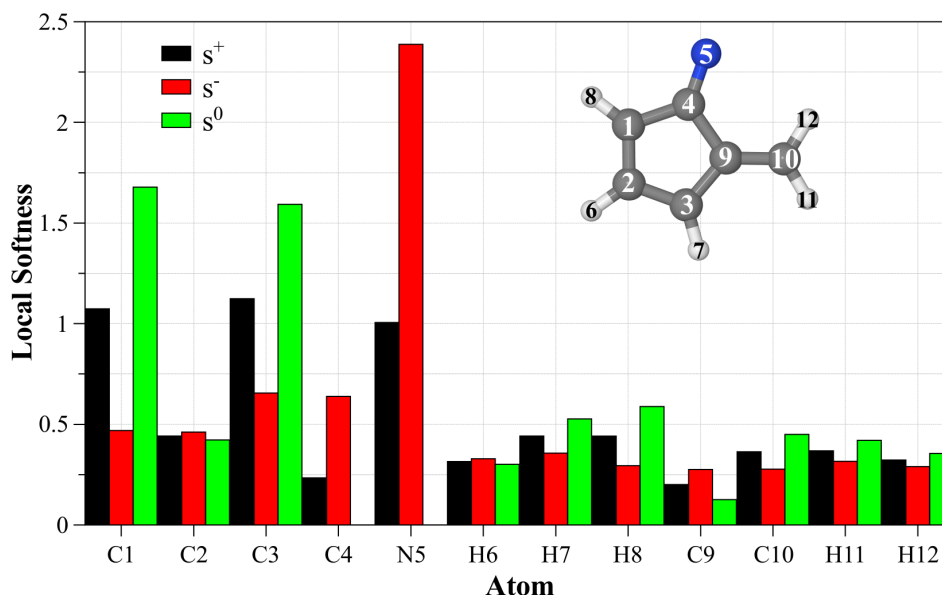
2.3.3. ALTERNATIVE ROUTES

As discussed above, although one complete pathway from 1-azafulvenallene to phenylnitrene was identified, several alternative routes were also found. In this section these routes are discussed, trying to verify if they can also lead to phenylnitrene. The analysis of these molecules remains the same combination of LS+IRI, in a DFT/B3LYP/6-311G(d,p) framework.

2.3.3.1. AZA-N

The first subject is Aza-N, the alternative route closest to phenylnitrene. This molecule comes from Aza-L by breaking the C1-N5 bond, which was identified by IRI analysis. Similarly to Aza-H, there are CS and OS structures for Aza-N, and although the LS are different, they yield to the same conclusions (paths). Figure 2.12 and Table 2.9 brings the results for its LS analysis (atomic charges included) for the CS structure. Results for OS structures are found in Appendix J.

Figure 2.12. Numbered structure for Aza-N (CS) and graph for local softness results.



Source: Author.

Table 2.9. ΔH , ΔE_T , S , LS and Q values for Aza-N (CS) atoms.

S	6.9893	$\Delta E_T(\text{kcal/mol})$	51.4	ΔH	3.5	Atom	Q
	s^+	s^-		s^0			
C1	1.6783	N5	2.3877	C3	1.1241	C1	0.0418
C3	1.5929	C3	0.6554	C1	1.0737	C2	-0.1063
C10	1.4303	C4	0.6387	N5	1.0057	C3	-0.0220
H8	0.5883	C10	0.5282	C10	0.9792	C4	-0.0618
H7	0.5268	C1	0.4691	C2	0.4418	N5	-0.3402
H11	0.4499	C2	0.4614	H7	0.4418	H6	0.1146
C2	0.4227	H7	0.3567	H8	0.4414	H7	0.1205

H12	0.4203	H6	0.3288	H12	0.3682	H8	-0.0814
H6	0.3013	H12	0.3161	H11	0.3635	C9	-0.0494
C9	0.1259	H8	0.2945	H6	0.3150	C10	0.1194
C4	0.0000	H11	0.2772	C4	0.2339	H11	0.1413
N5	0.0000	C9	0.2755	C9	0.2007	H12	0.1234

Source: Author.

There are two next to zero results, s_4^+ and s_5^+ . Both are, actually, negative values, around -0.3. These negative values come from the CAFI part of the LS, and they have no significant physical interpretation, and are set to zero. In CAFI they might be seen as indicative of non-optimal structure, which might be the case since these are, in general, transitional molecules.

Regarding both CTR and RR, there is a clear lead by C1/N5 interaction, which is the bond that needs to be broken to form Aza-N in the first place. Other than this interaction, there are also C3/C10 (CTR and RR) and C4/C10 (RR) interactions (C1/C3 and C3/N5 are chemically unfeasible). Both interactions build a bigger atomic ring, which might lead directly to phenylnitrene, though a middle point is also likely. Lastly, N5/C10 is also a possible interaction, which leads to a new molecule that drifts from the target, called Aza-N4. Table 2.10 summarizes the discussion above, bringing the compiled results as well as $\Delta s/\Sigma s$ and Eq. (2.8) parameters.

Table 2.10. Compiled results for Aza-N (CS) probable interactions.

Atoms	Int. Type	Δs	Σs	ΔQ	$\frac{\Delta s}{\Sigma s}$	$\frac{\Delta s}{\Delta Q * \Sigma s}$
C1/N5	s_1^+/s_5^-	0.7094	4.066	*	0.1745	*
	s_1^0/s_0^0	0.0680	2.0794		0.0327	*
C3/C10	s_3^+/s_{10}^-	1.0647	2.1211	*	0.5020	*
	s_3^-/s_{10}^+	0.7749	2.0856	*	0.3716	*
	s_3^0/s_{10}^0	0.1449	2.1034	*	0.0688	*
C4/C10	s_4^-/s_{10}^+	0.7916	2.0689	*	0.3826	*
N5/C10	s_5^-/s_{10}^+	0.9574	3.8180	*	0.2508	*
	s_5^0/s_{10}^0	0.0265	1.9850	*	0.0134	*

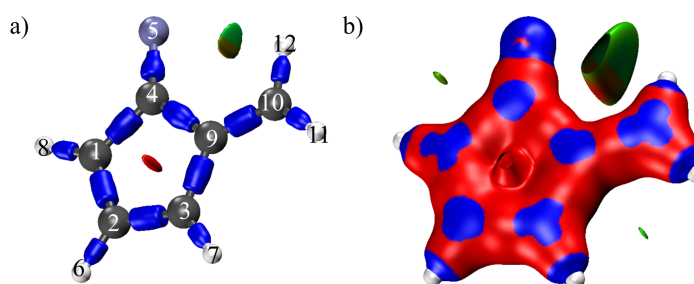
*atoms with same sign charges

Source: Author.

From Table 2.7 it's clear that RR is more advantageous for Aza-N, given the discrepancy in LS values: s_5^- is almost 50% greater than the highest s_n^+ , and about 4 to 5 times greater than the other s_n^- . These high LS values offer a higher Σs , which is a good metric, however is not enough to compensate for the great Δs . In short, among the selected options, the most prominent are N5/C10, C1/N5, and C3/C10. Taking only CTR into account, C1/N5 is the best option, followed by N5/C10.

The results point towards two main paths, Aza-N4 (from N5/C10), and back to Aza-L (from C1/N5). The paths that go towards Phenylnitrene (C3/C10 and C4/C10) are less likely. To observe other interactions, Figure 2.13 brings Aza-N's IRI results.

Figure 2.13. Aza-N's IRI result considering isovalue of a) 0.9, and b) 2.1.



Source: Author.

The IRI results also indicate a strong N5/C10, a relevant VdW interaction can be observed even at low isovalue (0.9). Besides that, no real indicator to strongly support other interactions. For the 2.1 isovalue figure, there are two very subtle VdW clouds between C1 and N5, and between C3/C10, which is consistent with the LS analysis. Moreover, the usual steric effect can be noticed in the center, which is responsible for hindering in-ring interaction such as C1/C3.

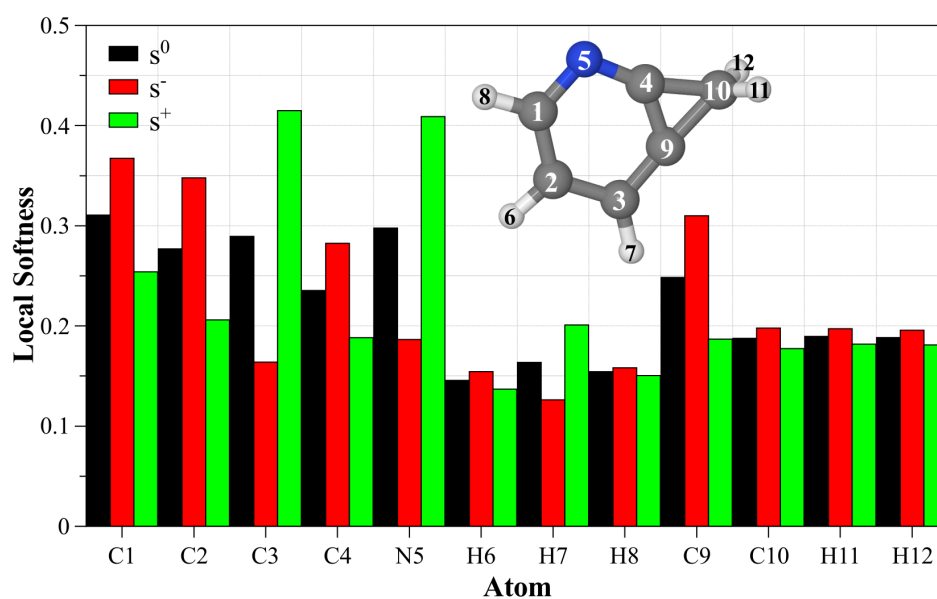
In summary, Aza-N combined results strongly point toward the Aza-N4 path, seemingly a dead end (see Appendix K). Its secondary pathway would be returning to Aza-L, which is positive, since from it there is an easy path towards phenylnitrene. Finally, there is slight chance of C3-C10 bonding, resulting in either a five-atom ring with a three-atom one connected to it (C3-C9-C10), or C10 being incorporated (as it is for Aza-W4, see Appendix K) into a six-atom ring, requiring a simple H movement to reach phenylnitrene.

2.3.3.2. AZA-O

The second subject is an alternative route from Aza-H, named Aza-O. This molecule is the result of Aza-H's C4-C10 atoms interacting. One might expect this interaction to result

in a seven-atom ring, however it actually built a three-atom cycle (C4-C10-C9), still requiring a bond-breaking interaction to achieve the aforementioned bigger ring. To verify the possibility of a new pathway towards phenylnitrene, this molecule was investigated by LS and IRI. Figure 2.14 and Table 2.11 brings the results for its LS analysis (atomic charges included) for the CS structure.

Figure 2.14. Numbered structure for Aza-O and graph for local softness results.



Source: Author.

Table 2.11. ΔH , ΔE_T , S , LS and Q values for Aza-O atoms.

S	2.6878	ΔE_T (kcal/mol)	15.9	ΔH	11.0	Atom	Q
	s^+	s^-		s^0			
C3	0.4149	C1	0.3674	C1	0.3107	C1	0.0296
N5	0.4090	C2	0.3478	N5	0.2977	C2	-0.1753
C1	0.2540	C9	0.3100	C3	0.2894	C3	-0.0257
C2	0.2060	C4	0.2825	C2	0.2769	C4	0.1002
H7	0.2010	C10	0.1979	C9	0.2484	N5	-0.2890
C4	0.1883	H11	0.1972	C4	0.2354	H6	0.1077
C9	0.1868	H12	0.1957	H11	0.1895	H7	0.1063
H11	0.1819	N5	0.1865	H12	0.1884	H8	0.1099
H12	0.1810	C3	0.1639	C10	0.1876	C9	-0.0719
C10	0.17738	H8	0.1582	H7	0.1636	C10	-0.1690

H8	0.1505	H6	0.1544	H8	0.1544	H11	0.1386
H6	0.1369	H7	0.1262	H6	0.1457	H12	0.1386

Source: Author.

The softest atoms vary according to the index +, - or 0. For s^+ they're C3 and N5, for s^- are C1, C2, C9, and C4. Finally, for s^0 presents C1, N5, C3, and C2 as the most relevant ones. Although numerous combinations are possible, the majority occur between already bonded atoms. The movement towards phenylnitrene requires breaking the C4-C9 bond, and bonding C1 with C4.

From the few non-bonded interactions, the ones with the highest LS values are C1/C3, and C2/N5. The combination of interest, C1/C4, is in the middle range of the LS, and might not be relevant. Table 2.12 brings the compiled results discussed and calculations of $\Delta s/\Sigma s$ and Eq. (2.8).

Table 2.12. Compiled results for Aza-O probable interactions.

Atoms	Int. Type	Δs	Σs	ΔQ	$\frac{\Delta s}{\Sigma s}$	$\frac{\Delta s}{\Delta Q * \Sigma s}$
C1/C3	s_1^-/s_3^+	0.0476	0.7823	0.0553	0.0608	1.1003
	s_1^0/s_3^0	0.0213	0.6001		0.0355	0.6418
C2/N5	s_2^-/s_5^+	0.0611	0.7568	*	0.0808	*
	s_2^0/s_5^0	0.0208	0.5746		0.0361	
C1/C4	s_1^-/s_4^+	0.0285	0.5365	*	0.0531	*
	s_1^0/s_4^0	0.0753	0.5461		0.1379	

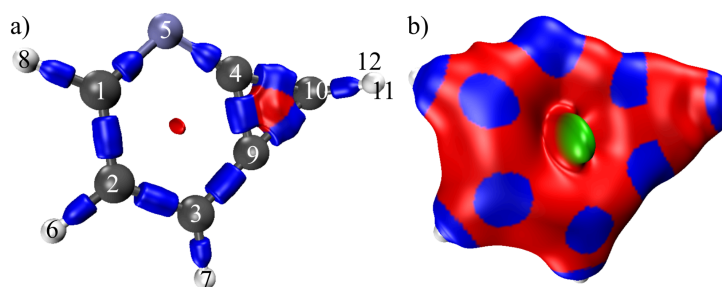
*atoms with same sign charges

Source: Author.

Both C1/C3 and C2/N5 presented relatively small $\Delta s/\Sigma s$, around the same value. For both RR is a more likely route. C1/C4 had a good CTR result, however not in pair with the previous two. It's important to highlight that all these interactions require going to a five-atom ring, seemingly drifting away from the target. The resulting molecule for C1/C3 interaction would likely have some symmetry with another small three-atom ring. Similarly, C2/N5 interaction could also result in a three-atom ring, or might expel C1 by breaking its bond to C2, leaving it connected to N5. Either way, both are quite far from the targeted molecule.

From the LS analysis, the sought after interaction is not the most likely, however it has some relevance. Figure 2.15 brings the IRI results, for a better understanding of the possible interactions.

Figure 2.13. Aza-O's IRI result considering isovalue of a) 0.9, and b) 2.5.



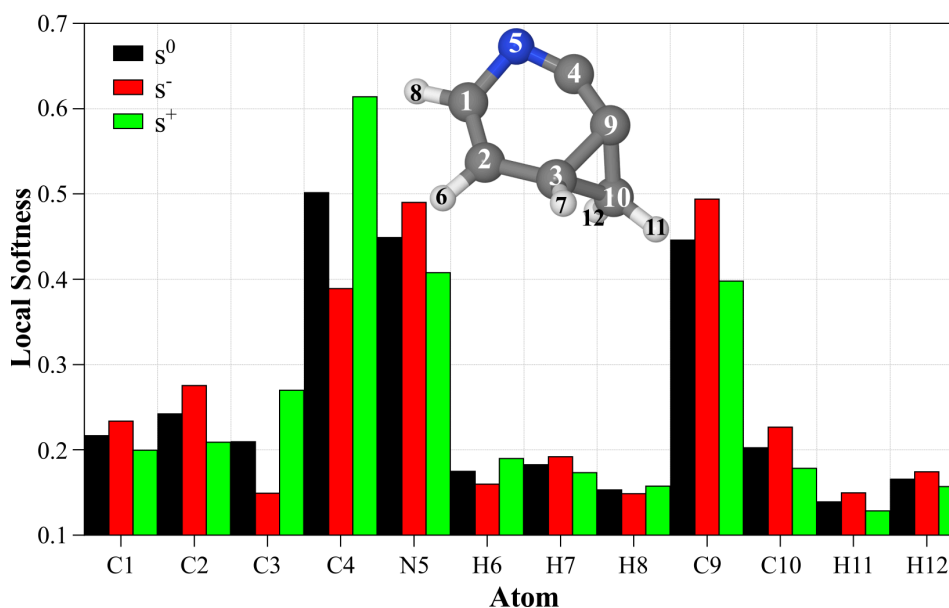
Source: Author.

Indeed the steric effect is concentrated in the center of the ring, however it's much stronger than what was observed for Aza-H. The other relevant information is the steric effect in the three-atom ring, which is strong and evenly distributed. This distribution makes it harder to predict which bond would break first (C4-C9, C4-10, or C10-C9). Therefore, the IRI result could be indicating a return to Aza-H, if C4-C10 breaks, going to a similar molecule to Aza-H in case C9-C10 breaks, or the formation of a seven-atom ring if C4-C9 breaks (Aza-W5 analogous, see Appendix J for Aza-W5 discussion).

Overall, LS and IRI studies for Aza-O are inconclusive. However, any of the three possible bond-breaking interactions looks promising. Returning to Aza-H allows it to follow the first found path. Becoming a seven-ring atom structure (similar to Aza-W5) is a plausible step towards the target molecule; this type of structure has been reported to reach phenylnitrene by C. Wentrup and M. S. Mirzaei (MIRZAEI; WENTRUP, 2023). The breaking of C9-C10 is a path yet to be explored, but given its similarities to Aza-H, it might still be a path towards the goal. Indeed, the same study from Wentrup and Mirzaei showed a similar molecule to what this result would be, requiring that a H atom moves C9, in that case, there is a path to phenylnitrene. Similarly, if instead of going back to Aza-H, one H moved to C4 (found by IRC as Aza-M), the study also showed a path to phenylnitrene (MIRZAEI; WENTRUP, 2023).

2.3.3.3. AZA-W4

From Aza-H there were three possible results, Aza-L (C1 bonds to C4), Aza-O (C4 bonds to C10), and Aza-W4 (C3 bonds to C10). The latter could only be identified by IRI results. Figure 2.14 and Table 2.13 brings the LS results for Aza-W4.

Figure 2.14. Numbered structure for Aza-W4 and graph for local softness results.

Source: Author.

Table 2.13. ΔH , ΔE_T , S , LS and Q values for Aza-W4 atoms.

S	3.0819	$\Delta E_T(\text{kcal/mol})$	51.1	ΔH	30.9	Atom	Q
	s^+	s^-		s^0			
C4	0.6139	C9	0.4939	C4	0.5015	C1	0.0126
N5	0.4077	N5	0.4901	N5	0.4489	C2	-0.1480
C9	0.3978	C4	0.3891	C9	0.4459	C3	-0.1270
C3	0.2698	C2	0.2754	C2	0.2422	C4	0.1684
C2	0.2089	C1	0.2337	C1	0.2166	N5	-0.2708
C1	0.1996	C10	0.2266	C3	0.2095	H6	0.1192
H6	0.1898	H7	0.1919	C10	0.2025	H7	0.1368
C10	0.1783	H12	0.1742	H7	0.1826	H8	0.1233
H7	0.1732	H6	0.1598	H6	0.1748	C9	-0.1261
H8	0.1574	H11	0.1496	H12	0.1656	C10	-0.1583
H12	0.1570	C3	0.1491	H8	0.1530	H11	0.1344
H11	0.1284	H8	0.1486	H11	0.1390	H12	0.1354

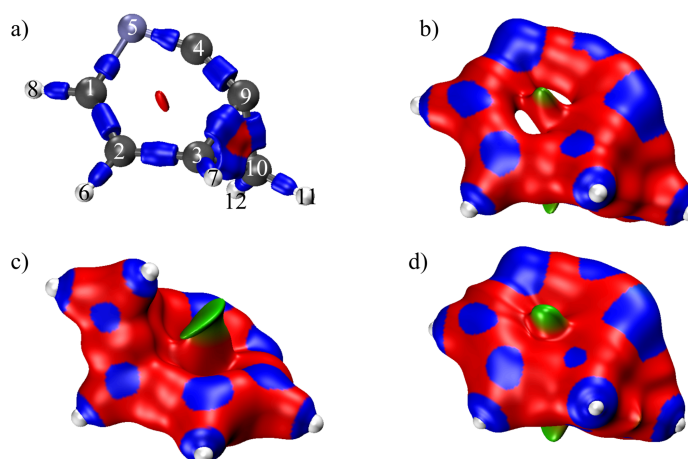
Source: Author.

Similarly to Aza-O's results, the combinations of the very soft atoms are between already bonded atoms (C4, N5, and C9). Moreover, outside the three most soft atoms, the

other atoms' softs stay around half of the highest softness of any of three indexes, which makes it unlikely to have new interactions. The most sought after steps are the C3-C9 bond breaking interaction, which will be verified by IRI, but can't be by LS analysis, and the other interaction is between C1 and C4, to position N5 outside the ring, approaching phenylnitrene structure. This interaction can be seen in the table and graphic, however it's not relevant, as C1 is particularly hard.

For this particular structure, LS provides no pathway, it's a stable molecule regarding softness. To try to access new pathways, Figure 2.15 brings the IRI results for Aza-W4.

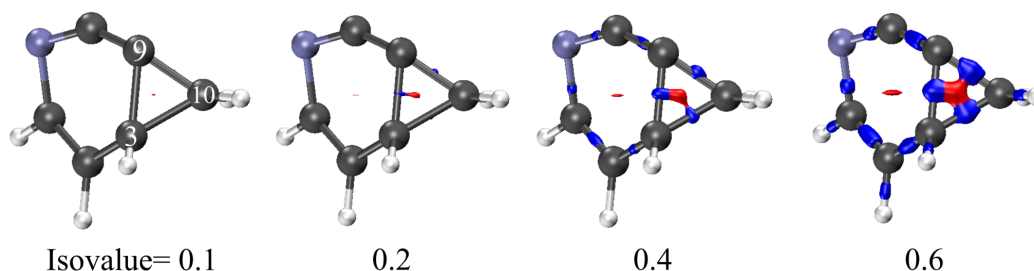
Figure 2.13. Aza-W4's IRI result considering isovalue of a) 0.9, b) 2.1, b) 2.1 lateral view, and d) 2.5.



Source: Author.

As usual, the inner region of the ring has a repulsive steric effect, however even for a larger (2.1) isovalue, there are regions with reduced steric effects, allowing in-ring interaction. A possible interaction would be N5-C9, which is actually supported by LS results, but would lead nowhere closer to the target. Another important observation is the repulsive interaction in the smaller ring, which appears to be a strong effect. Even in smaller isovalues (0.2) this steric effect is already apparent. Similarly to Aza-O, it's not possible to safely argue which of the three bonds might break due to this effect. Conversely, when exploring smaller isovalues, it's possible to observe that this effect starts at the center of the three-atom ring, and is quickly connected to C3-C9 bond, then to C3-C10, Figure 2.14 illustrates this smaller isovalues.

Figure 2.13. Aza-W4's IRI isosurface evolution considering small isovalues.



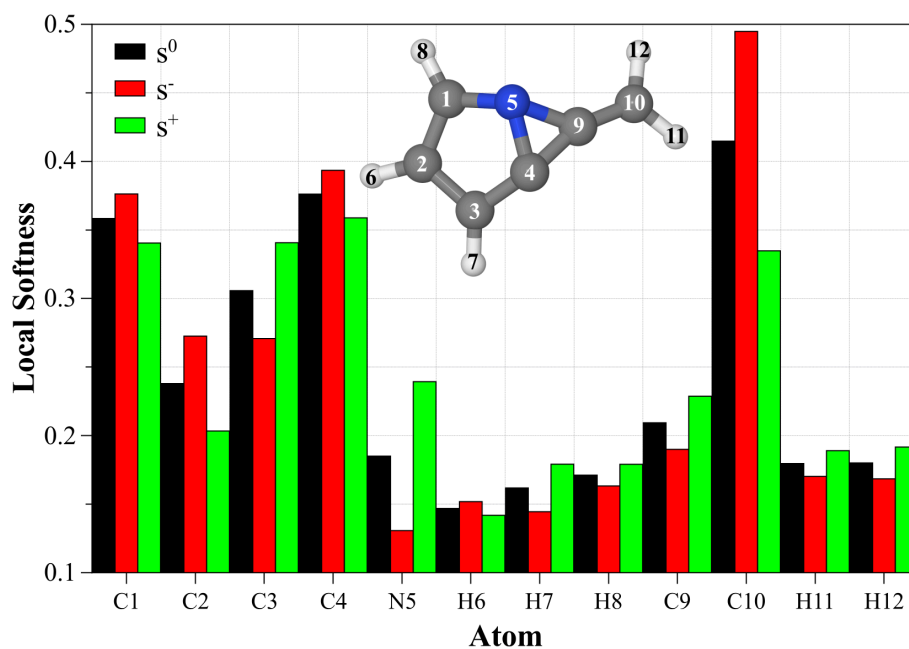
Source: Author.

The way the repulsive interaction evolves for bigger isovalues might be indicating the places it has stronger effect, being the C3-C9 bond. Secondly, the repulsive interaction reaches the C3-C10 bond. The result of these bond-breaking interactions are the formation of a seven-atom ring molecule (found by IRC as Aza-W5 and Aza-W3), and regressing to Aza-H, respectively.

In conclusion, the Aza-W4 was one the most difficult molecules to analyze. From its LS results, the only possible interaction would be N5-C9, which drifts it away from the target molecule. Conversely, with a deep analysis of IRI results, testing different ranges of isovalues, it was possible to verify other two paths, one back to Aza-H (which can follow the regular pathway), and one to Aza-W5/-W3.

2.3.3.4. AZA-G

The last alternative path to be analyzed is Aza-G, this molecule is the result of C9/N5 interaction from 1-azafulvenallene, presenting good LS and IRC, but behind Aza-H for IRI analysis. Figure 2.14 brings the LS values results and the numbered structure of Aza-G. Table 2.14 summarizes these results.

Figure 2.14. Numbered structure for Aza-G and graph for local softness results.

Source: Author.

Table 2.14. ΔH , ΔE_T , S , LS and Q values for Aza-G atoms.

S	2.9268	$\Delta E_T(\text{kcal/mol})$	35.1	ΔH	37.9	Atom	Q
	s^+	s^-		s^0			
C4	0.3588	C10	0.4948	C10	0.4148	C1	0.0192
C3	0.3407	C4	0.3935	C4	0.3761	C2	-0.1544
C1	0.3405	C1	0.3762	C1	0.3584	C3	-0.1008
C10	0.3348	C2	0.2726	C3	0.3057	C4	0.0010
N5	0.2393	C3	0.2708	C2	0.2380	N5	-0.2300
C9	0.2287	C9	0.1900	C9	0.2093	H6	0.1009
C2	0.2034	H11	0.1702	N5	0.1850	H7	0.1091
H12	0.1917	H12	0.1685	H12	0.1801	H8	0.1179
H11	0.1890	H8	0.1633	H11	0.1796	C9	0.1390
H7	0.1791	H6	0.1518	H8	0.1712	C10	-0.2546
H8	0.1791	H7	0.1445	H7	0.1618	H11	0.1262
H6	0.1419	N5	0.1307	H6	0.1468	H12	0.1265

Source: Author.

Aza-G's LS result is dominated by C10, C4, and C1 (C3 is also relevant for s^+). One of the main interactions raised by this result is C4/C10, basically all others are unlikely given their distance (C1/C10, C3/C10), or because would result in a four-atom ring (C1/C3, and C1/C4). Table 2.15 brings the C4/C10 interaction analysis.

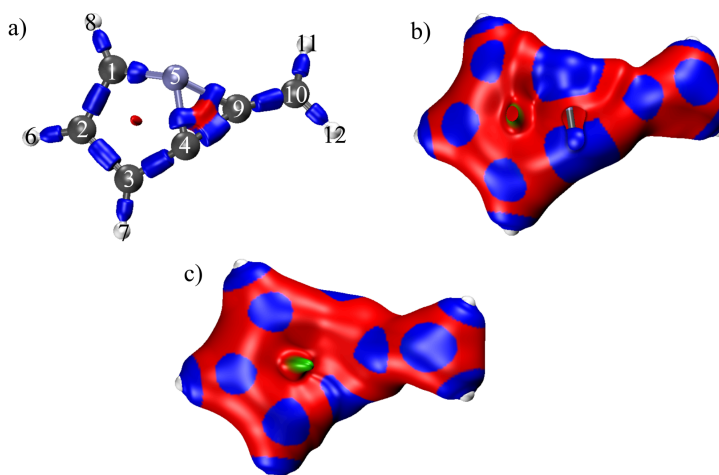
Table 2.15. Compiled results for Aza-G probable interactions.

Atoms	Int. Type	Δs	Σs	ΔQ	$\frac{\Delta s}{\Sigma s}$	$\frac{\Delta s}{\Delta Q * \Sigma s}$
C4/C10	s_4^+/s_{10}^-	0.1360	0.8536	0.2556	0.1593	0.6232
	s_4^-/s_{10}^+	0.0587	0.7283		0.0806	0.3153
	s_4^0/s_{10}^0	0.0386	0.7909		0.0488	0.1910

Source: Author.

This interaction is interesting for both CTR and RR. The results for the RR, however, are much lower, which is better. This reaction points to a movement towards building a bigger ring molecule (see Aza-W3, Appendix J), considering C4-N5 bond breaking. To verify the breaking possibility, IRI analysis was performed, the results are presented on Figure 2.15.

Figure 2.15. Aza-G's IRI result considering isovalue of a) 0.9, b) 2.5, b) 2.5 back view..



Source: Author.

Differently from other molecules with a 3-atom “ring”, here the steric effect is asymmetric, expected given the presence of N5, instead of 3 C atoms. The attractive interaction is quite strong in C4-C9 bond, and weaker for all N5 bonds, likely related to its extreme hardness (s_5^- is the smallest LS value). At this point it might seem possible that any of N5's bonds could break, however the repulsive interactions point otherwise. Notice how (a)

the repulsive clouds are concentrated around C4 and C9, and from (b) and (c) there is a bulge around the N5-C9 bond. Together, these observations points towards three possibilities: *i*) going back to 1-azafulvenallene by breaking N5-C9; *ii*) going to a six-atom ring molecule, similar to Aza-H; *iii*) C4-C9 bond breaking, leading to a structure that resembles 1-azafulvenallene itself. These are possibilities yet to be explored through IRC and LS+IRI analysis.

2.3.4. RELATIONSHIP BETWEEN ENTHALPY OF FORMATION (IRC DATA) AND LS DATA

At its core, LS analysis uses the HSAB principle to predict intermolecular interactions between two atoms j and k , considering their local softness. From this principle, the interaction is more likely to take place between soft atoms, with similar softness degree. To account for the highest softness, $\Sigma s = s_j + s_k$ was considered. On the other hand, the similarity was measured as $\Delta s = |s_j - s_k|$. These two magnitudes were capable of being defined as very likely interactions, the ones found by IRC as the least energetic to achieve (ΔH).

Despite the aforementioned success, a correlation between LS analysis and ΔH was not made. In this section we set out to explore potential relationships between LS derived magnitudes and ΔH . Table 2.16 brings a compilation of LS results and enthalpy of formation found by IRC provided by Prof. Didier Bégué.

Table 2.16. LS and IRC relevant data for correlation from 1-azafulvenallene to phenylnitrene (here Aza is short of 1-azafulvenallene).

Start	Finish	Int. Type	$\frac{\Delta s}{\Sigma s}$	$\frac{\Delta s}{\Delta Q \cdot \Sigma s}$	in-ring	ΔH	$\frac{\Delta H}{\frac{\Delta s}{\Sigma s}}$
Aza	Aza-H	s_3^-/s_9^+	0.1761	0.6707	NO	45.5	258.4
	Aza-G	s_5^-/s_9^+	0.1662	0.3453	NO	37.9	228.0
	Aza-I	s_2^-/s_5^+	0.2431	*	YES	122.2	502.7
		s_2^0/s_5^0	0.0290				4213.8
	Aza-B	s_3^0/s_5^0	0.0208	*	YES	92.3	4437.5
Aza-H	Aza-O	s_4^-/s_{10}^+	0.0432	0.1450	NO	11.0	254.6
	Aza-L	s_1^-/s_4^+	0.0806	*	YES	22.0	273.0
	Aza-W4	s_3^+/s_{10}^-	0.3592	*	NO	30.9	86.0
		s_3^-/s_{10}^+	0.3948		NO		78.3
		s_3^0/s_{10}^0	0.3230		NO		98.7

Aza-L	Aza-P*	s_3^-/s_{10}^+	0.1789	*	NO	no data
	Aza-P	s_4^+/s_{10}^-	0.0293	0.1661	NO	

*atoms with same sign charges

Source: Author.

Considering the first two rows, Aza-H and Aza-G, there is a seemingly consistent proportionality between $\Delta s/\Sigma s$ and ΔH (looser if considered ΔQ), a slight difference between the LS magnitudes leads to a slight different enthalpy. Conversely, when considering Aza-I and Aza-B, very low $\Delta s/\Sigma s$ is found, inconsistent with their high ΔH . The explanation to this phenomenon is likely an overestimation of LS for in-ring/in-ring atoms interaction, and/or overestimation of RR.

For Aza-H pathways, Aza-O and Aza-L show approximately a two times difference in $\Delta s/\Sigma s$, and exactly two times difference in ΔH . Here, both are CTR, however Aza-L comes from an in-ring/in-ring interaction, but no overestimation is observed. The reason might be that for Aza-L it's a transition from a 6- to a 5-atom ring, unlike Aza-B and -I which goes from 5- to 4-atom ring (high energetic cost). Moreover, to be truly consistent, the $\Delta s/\Sigma s$ for Aza-W4 should be around 50% higher than Aza-L's, but it's four times bigger (even considering its RR). The latter reaction seems to be a strong argument against RR being overestimated.

The last column in Table 2.16 brings a ratio between the two main magnitudes for ease of interpretation. From this column one can see that the paths from 1-azafulvenallene to Aza-H and Aza-G, and from Aza-H to Aza-O and Aza-L, present a similar ratio (~ 250), while the rest diverge significantly. In relation to the divergent results, for Aza-B and Aza-I it seems the major obstacle was not accounting for the ring-size reduction to a 4-atom ring, which requires significant energy. For Aza-W4, on the other hand, the problem might be a shortcoming of LS. The interaction to build Aza-W4 is C3/C10, which would not be chosen as very likely solely by LS as C3 is very close in softness to some H atoms (that are hard), however IRI pointed to this possibility. Indications are that LS analysis can't be consistent for harder atoms, only the softest ones.

In short, correlation between LS magnitudes and IRC-found ΔH is somewhat consistent when considering $\Delta s/\Sigma s$ and only the softest atoms in the molecule. Notice that difference in charge was disregarded as throughout the path, it is not relevant since many interactions happened independent of the atomic charge. It must be said that this section relies on a very small dataset. Further studies with different 1-azafulvenallene pathways, and

especially with different molecules, are necessary to verify how other variables might affect (in-ring interactions, RR or CTR, distance, etc).

2.4. CONCLUSIONS OF THE CHAPTER

In this chapter, two complete pathways from 1-azafulvenallene to phenylnitrene could be found by LS and IRI analysis. These tools are computationally inexpensive and proved invaluable in this research area, positioning themselves as a cost-efficient tool in relation to alternatives such as the IRC study. The results from LS are aligned with IRC, and there is a relation between LS's $\Delta s/\Sigma s$ and IRC's enthalpy of formation.

The first pathway was completely found by either LS, IRI, or a combination of both results, guided by IRC-found structures. It starts at 1-azafulvenallene, to Aza-H, Aza-L, Aza-P, and then to phenylnitrene. This path has some alternative routes, some of which also go to the targeted molecule.

A secondary complete path was also found as: 1-azafulvenallene, Aza-H, Aza-W4, Aza-W5, Aza-W3, and then phenylnitrene. However, from Aza-W5 to Aza-W3 there is an H atom movement that couldn't be predicted by the proposed tools, only by IRC.

In general, LS+IRI is capable of finding a myriad of relevant interactions. The LS part of the analysis indicates quantitatively which two atoms i and j are the most likely to interact (either CTR or RR) by considering their difference in LS (Δs) and how soft they are (Σs). The IRI aids the LS analysis by making steric effects, Van der Waals, and attractive interactions explicit, which helps finding bond-breaking interactions and deciding between two attractive interactions. Conversely, even the combination of both methods is insufficient to identify H-atom interactions.

The proposed methodology consists of finding the most likely to interact atom via LS+IRI analysis, and execute it via IRC calculation, avoiding the waste of computational resources. Although LS+IRI indicates the pathway, the actual structure resulting from such interaction must be appropriately calculated via a reliable method, such as IRC.

Regarding the correlation between LS and enthalpy, a direct and consistent relation was not found. In fact, $\Delta s/\Sigma s$ is indeed proportional to ΔH , but it is only consistent for interactions between the softest atoms. This approach also disregards strong steric effects and structural barriers. However, even with these shortcomings, it is sufficiently good to find the best pathways consistent with IRC studies.

In conclusion, LS proved to be an inexpensive and efficient tool to track intramolecular interactions, capable of predicting chemical pathways. The IRI analysis

complements LS by tracking steric effects and attractive interactions, indicating bond-breaking reactions. Together, they are capable of finding complete pathways, relying on IRC to find the actual realistic result from a predicted interaction.

CONCLUSIONS OF THE THESIS

In the present work, theoretical computational studies were made for two distinct systems of interest in two different methodologies: *i*) donor and acceptor materials suitable for OSC active layer application and what makes them build a highly efficient device, and *ii*) 1-azafulvenallene and its pathways to phenylnitrene, investigated via local softness descriptors and IRC.

In the first chapter, electronic structure data, such as MEP and CAFE, were used to investigate the charge transfer and charge transport processes at the molecular level in BHJOSC. These studies were applied to: *i*) very successful donor:NFA pairs, e.g. PM6:Y6 and D18:Y6; *ii*) to the first introduced A-DA'D-A NFA, BZIC, and its pair HFQx-T; and *iii*) to the widely studied fullerene-based pair, P3HT:PCBM. The studies allowed us to trace the difference in molecular properties of these pairs, and thus identify some desirable features in donors/acceptors to build highly efficient OSCs. The main relevant properties are: *i*) good donor characteristics in the acceptor, *ii*) good acceptor characteristics in the donor, *iii*) f^+ and f^- sites alignment in the stacked structure, and *iv*) alignment of positive (negative) MEP with f^+ (f^-). Moreover, a tool for charge transfer study (CTFI) in dimeric systems was developed and applied to Y6 dimers, allowing for a deep verification and understanding of possible charge transfer routes.

In the second chapter, it was possible to verify the quality of the computationally inexpensive descriptor (LS) applied in the investigation of intramolecular interactions. In this application, LS results point in the same direction as the more complex and computationally expensive method, IRC. This study was applied to the 1-azafullvenallene in search of its pathway to become phenylnitrene. During this process, shortcomings in the LS analysis appeared, which allowed to define the ideal situations to use such a tool. Moreover, an initial correlation equation was set, saying that (ICR derived) ΔH is somewhat proportional to $\Delta s/\Sigma s$.

Although the areas of knowledge and science in these chapters are quite different, both made use of cheap tools to study important and complex subjects. The first one directly used the CAFE, a reactivity tool as a means of understanding the charge transference and transportation on the molecular scale. The second combines CAFE with global softness to use the LS index, which is also usually used as a reactivity tool. However, it was used to find intramolecular interactions and build chemical pathways. In conclusion, this work shows how relevant simple and cheap reactivity descriptors can be with the proper use and clever interpretation.

PUBLICATION LIST

Published articles:

- CUBA, P. B. J.; ALVES, G. G. B.; GALINDO, L. A.; PAULIN, J. V.; BATAGIN-NETO, A. Sulfonated melanin derivatives: theoretical evaluation of local reactivities and chemical structures. *JOURNAL OF MOLECULAR MODELING*, v. 27, p. 1-8, 2021.
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- ALVES, G. G. B.; BÉGUÉ, D.; BATAGIN-NETO, A. Reactivity-Based Descriptors for Donor-Acceptor Efficiency in Organic Solar Cells. *COMPUTATIONAL AND THEORETICAL CHEMISTRY*, Submitted, 2025. (Preprint available: <http://dx.doi.org/10.2139/ssrn.5147455>)

Articles being written:

- CACHANESKI-LOPES, J. P.; ALVES, G. G. B.; BÉGUÉ, D.; BATAGIN-NETO, A. DFT-Guided Design of Melanin-Inspired Materials for High-Performance Organic Solar Cells.
- SILVA, F. G.; ALVES, G. G. B.; GALINDO, L. A.; BATAGIN-NETO, A. Molecular modeling of covalent organic structures: substituent effects study.
- ALVES, G. G. B.; BÉGUÉ, D.; WENTRUP, C.; BATAGIN-NETO, A. Chemical Routes from 1-Azafulvenallene to Phenylnitrene Through Weak-Interaction Indicators.
- ALVES, G. G. B.; BÉGUÉ, D.; WOELLNER, C. F. BATAGIN-NETO, A. Y6-Y6 Charge Transference Unveiled via Condensed-to-Atoms Charge Transfer Fukui Indices and Percolation Theory.

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APPENDIX A. HISTORICAL DEVELOPMENT AND BASIC ASPECTS OF THE DENSITY FUNCTIONAL THEORY

The main results herein presented were obtained via electronic structure calculation in a density functional theory (DFT) framework. Unlike other methods, DFT does not rely on the wave function concept, but on electronic density, defined as the probability of finding electrons per unit of volume (LEWARS, 2016). The basis for this theory was the proof by Hohenberg and Kohn that there exists an one-to-one correspondence between the electron density and the energy of a given system (JENSEN, 2017). That means a system's properties may be expressed as a function of the observed electronic spatial distribution, $\rho(x,y,z)$ (LEWARS, 2016). In this appendix a general historical evolution of the theory is presented, no intention of proving or further developing presented equations. One may want to delve deeper into it, therefore the bibliography referenced herein is recommended, such as "Introduction to Computational Chemistry" by Frank Jensen, and "Computational Chemistry" by Errol G. Lewars for a more straightforward development or "Density-Functional Theory of Atoms and Molecules" by Robert G. Parr and Weitao Yang for more details about earlier models.

In fact, materials' properties analysis considering electron density began around the beginning of the 20th century, with Drude's theory for metals. However, only with Llewellyn Thomas and Enrico Fermi contributions in 1927 and 1928, respectively, did DFT start to take form as it is known today (FERMI, 1927; THOMAS, 1927). From the consideration of an electron gas, these authors manage to get to the same result, independently. Nowadays, the approach is known as Thomas-fermi functional (TF) and proposes a kinetic energy functional dependent of electronic density given by (in atomic units) (JENSEN, 2017):

$$T_{TF}[\rho(\mathbf{r})] = C_F \int \rho^{5/3}(\mathbf{r}) d\mathbf{r}, \quad C_F = \frac{3}{10}(3\pi^2)^{2/3} \quad (\text{A.1})$$

Considering the classical expressions for nuclei-electron and electron-electron interactions, respectively, it is possible to express an atom energy as a functional of $\rho(\mathbf{r})$:

$$E_{TF}[\rho(\mathbf{r})] = C_F \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} - \sum_a^{N_{nuclei}} \int \frac{Z_a(\mathbf{R}_a)\rho(\mathbf{r})}{|\mathbf{R}_a - \mathbf{r}|} d\mathbf{r} + \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (\text{A.2})$$

Despite its historic relevance, (A.2) wasn't capable of describing limited systems properties appropriately. Moreover, it presents incorrect assistontic behavior for $\rho(\mathbf{r})$ when $\mathbf{r}$ tends to zero or infinity.

Due to said problems with TF functional, many corrections were proposed, among them Paul Dirac's was one of the most important (DIRAC, 1930). Dirac's correction consisted in inserting an exchange term to correct self-interaction problems from classical electron interaction expressions. It also considered the total electron exchange energy, associated with Pauli's principle (JENSEN, 2017; LEWARS, 2016). The result is known as Thomas-Fermi-Dirac functional (TFD) (JENSEN, 2017):

$$E_{TFD}[\rho(\mathbf{r})] = E_{TF}[\rho(\mathbf{r})] - C_X \int \rho^{4/3}(\mathbf{r}) d\mathbf{r}, \quad C_X = \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \quad (\text{A.3})$$

TFD functional is based on an uniform electron gas analysis, therefore approximations for kinetic energy and exchange functionals consider a small volume element (local wave vector). Thus, this functional is considered a local density approximation (LDA). This characteristic makes it difficult to describe electron density inhomogeneity that is naturally expected in atoms and molecules. To try making up for this shortfall, additional corrections by Weizsäcker were considered, better representing the mentioned inhomogeneity (LEWARS, 2016; PARR; YANG, 1994; WEIZSÄCKER, 1935).

Many other models had been implemented to enhance previous models' quality. In general, many of these approaches were not successful for chemical applications. The actual next step towards DFT were the theorems by P. Hohenberg and W. Kohn, known as the Hohenberg-Kohn (HK) theorem (HOHENBERG; KOHN, 1964). There are two HK theorems, the first one says that a molecule's total energy (and therefore other properties) at the ground state can be measured by the electronic density function of said state, *i.e.*, the system's energy could be expressed as a electronic density functional (LEWARS, 2016):

$$E_0 = E[\rho_0] \quad (\text{A.4})$$

The second theorem says that any trial electron density function will lead to an equal or higher energy value than the real ground state one. That means only ρ_0 can describe an electronic distribution that leads to an energy minimum E_0 ($E[\rho_0] \leq E[\rho]$) (JENSEN, 2017; LEWARS, 2016).

Equation (A.4) represents the ground state system's total energy as an electronic density functional, such that each component also have to show the same dependence (PARR; YANG, 1994):

$$E[\rho] = T[\rho] + E_{e-e}[\rho] + E_{N-e}[\rho], \quad (\text{A.5})$$

where T represents electrons' kinetic energy, E_{e-e} represents interaction between electrons and E_{N-e} represents nuclei electrons interaction. Also, (A.5) can be simplified by unifying T and

E_{e-e} as an external potential independent part F_{HK} , the HK functional. This way the following equations can be written (PARR; YANG, 1994):

$$F_{HK}[\rho] = T[\rho] + E_{e-e}[\rho] \quad (\text{A.6})$$

$$E_{N-e}[\rho] = \int \rho(\mathbf{r}) V_{N-e} d\mathbf{r} \quad (\text{A.7})$$

$$E[\rho] = F_{HK}[\rho] + E_{N-e}[\rho] \quad (\text{A.8})$$

As can be seen, the nuclei-electrons interaction term has an explicit form (A.7), while for kinetic and electron-electron interaction energies such a form is unknown. Notice that, from the theorems, once F_{HK} is known, it is possible to exactly solve Schrödinger's equation (SE) for any given system, due to the fact that such a function is independent from the considered system's spatial arrangement.

However, as for the moment there is no exact description of F_{HK} , some approximations have to be made to compute it. For instance, considering TFD-based functionals, it's made clear that $E_{e-e}[\rho]$ can be divided in, at least, two parts that represent Coulomb's interaction ($J[\rho]$) and non-classical correction for self-interactions, such as correlation and exchange effects ($V^{nc}[\rho]$). All together:

$$E_{e-e}[\rho] = J[\rho] + V_{e-e}^{nc}[\rho] \quad (\text{A.9})$$

Some similar non-classical corrections were also applied to TF and TFD functionals. However these approaches were not enough to make up for their flaws (LEWARS, 2016; PARR; YANG, 1994).

Considering equation (A.6), the other term to be adjusted is $T[\rho]$, which is still the same from the TF model, and is inaccurate for most applications, even after Weizsacker's corrections. The correction that finally circumvented this problem came with W. Kohn and L. Sham equations in 1965 (KOHN; SHAM, 1965).

The Kohn-Sham (KS) approach divided the kinetic energy into two parts, such that it is possible to define a reference system, without interactions, T_r , which shows the same electronic density ρ_r that the real interacting system ρ , given by (LEWARS, 2016):

$$T_r[\rho] = \left\langle \psi_r \left| \sum_i^{2n} -\frac{1}{2} \nabla_i^2 \right| \psi_r \right\rangle = -\frac{1}{2} \sum_i^{2n} \langle \chi_i^{KS}(1) | \nabla_1^2 | \chi_i^{KS}(1) \rangle, \quad (\text{A.10})$$

where the sum goes over the $2n$ electrons in the system and ψ_r represents the reference system's multi electron ground-state wavefunction, made by a single Slater determinant [lewars 2016]. On the rightmost side of the equation, χ_i^{KS} represents the i -th KS spin orbital

of an electron in the reference system (that's part of ψ_r 's Slater determinant). Equation (A.10) functionals can be justified if (JENSEN, 2017; LEWARS, 2016):

$$\rho = \rho_r = \sum_i^N |\chi_i^{KS}(1)|^2 \quad (\text{A.11})$$

It is important to highlight that what is presented in (A.10) does not imply that DFT is based on wavefunctions, KS orbitals are just a mathematical tool that allows us to estimate a major part of the system's kinetic energy more precisely.

Given (A.9) and (A.10), there is a approximated way to derive $F_{HK}[\rho]$:

$$F_{HK}[\rho] = T_r[\rho] + J[\rho] + E_{XC}[\rho], \quad (\text{A.12})$$

where the term E_{XC} carries all unknown information about the real system: non-classical corrections associated with potential energy (self-interaction and exchange and correlation effects between electrons) as well as the residual part of the real kinetic energy that could not be well described by T_r . It is generically called XC functional. Mathematically this term can be represented by the following (JENSEN, 2017):

$$E_{XC}[\rho] = (T[\rho] - T_r[\rho]) + (E_{e-e}[\rho] - J[\rho]) = T_C[\rho] + V_{e-e}^{nc}[\rho] \quad (\text{A.13})$$

Using (A.12) in (A.8) is possible to build a new total energy equation as follows:

$$E[\rho] = T_r[\rho] + J[\rho] + E_{N-e}[\rho] + E_{XC}[\rho] \quad (\text{A.14})$$

As expected, this equation is very similar to (A.5), it basically brings the same terms, however everything that is of difficult description is concentrated in E_{xc} . This makes sure that everything but the XC functional can be exactly computed. This functional is of extreme relevance to DFT, some of its basic aspects are presented in Appendix B.

APPENDIX B. EXCHANGE AND CORRELATION FUNCTIONAL

Appendix A brought the historic development of DFT equations, finalizing with equation (A.14), which defines explicitly the XC functional E_{XC} , the energy parcel that cannot be exactly calculated and accumulates non-classical corrections and other complicated to compute terms. Given this complicated nature, it is a great challenge to describe it.

To mitigate this difficulty a diverse set of approximations were proposed throughout the years, the simplest one is the aforementioned LDA. It is applied for situations where the electronic cloud has little variation with spatial position (like mentioned for TFD functional), therefore it considers only the conditions in the very vicinity of each point. Another similar method is the local spin density approximation (LSDA). The advantage of this approach is being able to better describe systems with one or more unpaired electrons and systems where the electrons become unpaired, for instance, molecules outside of its geometric equilibrium. For perfect paired systems (closed-shell), LSDA and LDA are pretty much equivalent (JENSEN, 2017; LEWARS, 2016).

The aforementioned approximations start from somewhat unrealistic consideration, given that, in general, electron density in atoms/molecules does vary with position. Therefore, corrections were necessary to enhance application capabilities, a way to do it is to add an electron density gradient. This correction is known as generalized-gradient approximation (GGA) method, sometimes referred to as non-local methods (JENSEN, 2017; LEWARS, 2016).

For all previous approximations, XC functional is often divided in two, the exchange (E_X) and the correlation (E_C) part:

$$E_{XC}[\rho] = E_X[\rho] + E_C[\rho] \quad (\text{B.1})$$

It is important to highlight that, in general, $|E_X|$ is way bigger than $|E_C|$. For instance, argon's values for exchange and correlation energies are $-30.19 E_h$ and $-0.72 E_h$, respectively. One is not even 3% of the other, such a big difference makes it more efficient to use GGA to correct E_X (LEWARS, 2016).

Throughout the years of development, one major step towards nowadays accurate DFT calculation was Becke 88 (B88) functional introduction (BECKE, 1988). This functional describes E_X (the major part of E_{XC}). Other important advancements were made in relation to E_C (GGA considered), namely Lee-Yang-Parr (LYP) and Perdew 1986 (P86) (LEE; YANG;

PARR, 1988; PERDEW, 1986). Both commonly used with gaussian functions represented KS orbitals.

Hybrid functionals are another kind of XC functional, it enhances DFT E_{XC} with an *ab initio* term from Hartree-Fock (HF) theory (KOHN; SHAM, 1965; LEWARS, 2016). Such a term comes from the HF electronic energy. When eliminating coulomb interactions, kinetic energy and nucleus-electron attraction from this energy, the leftovers are exchange integrals that are then applied to KS orbitals. The result is a functional capable of describing a system of non-interacting electrons with an electron density equal to the real system (precision limited to the chosen function basis set 's quality) (CRAMER, 2004; LEWARS, 2016).

Nowadays, one of the most widely used (also used in this work) hybrid functional is called B3LYP. This functional is based on the E_X developed by Becke in 1993, modified by Stephens *et al.* in 1994 with LYP E_C , and can be mathematically expressed as:

$$E_{XC}^{B3LYP} = (1 - a_0 - a_X)E_X^{LSDA} + a_0E_X^{HF} + a_XE_X^{B88} + (1 - a_C)E_C^{VWN} + a_CE_C^{LYP} \quad (B.2)$$

For this functional, the E_X^{LSDA} part represents the local parcel, without GGA, the E_X^{HF} and E_X^{B88} parts are the ones just discussed above, E_C^{VWN} is the Vosko Wilk Nusair function that makes part of the accurate functional for homogeneous electron gas for LDA and LSDA and E_C^{LYP} is the one discussed above. The last three terms of (B.2) are GGA corrected. The three parameters shown (*a*) in the equation are those that give the best fit of calculated energy in relation to the molecular optimization energies, and thus the reason for the “three parameter” in B3LYP’s full name (Becke, 3-parameter, Lee-Yang-Parr).

APPENDIX C. BASIS SET

In the main text and previous appendices the term “basis set”, a set of basis functions (also called atomic orbitals), can be found several times and it is crucial for most modern electronic structure calculations. A basis set is an optimized linear combination of multiple mathematical functions that allows for a good representation of the molecular orbitals of a given material. These linear combinations of wave functions have their coefficients derived from variational methods (aiming for energy minimization).

There are a variety of basis sets, showing different complexity and accuracy, which are used in different applications. Although there are many basis sets, these sets are built by either slater-type orbitals (STO) or Gaussian-type orbitals (GTO). Among the simplest basis sets are the ones applied in methods such as Hückel’s method, which just consist of p_z orbitals associated with the valence orbitals; it’s neither STO nor GTO. There is no concern to the mathematical shape of the functions, reducing interactions to first neighbors and previously tabled energy parameters (JENSEN, 2017; LEWARS, 2016).

The simplest utilized basis set is STO-3G (STO approximated by three gaussians), a small base of reduced accuracy. STO-3G utilizes one function for each s -type orbital, three for each p -type (p_x , p_y and p_z) and five for each d -type (d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$ and d_{z^2}). It also introduces the concept of contraction shells, building its contracted gaussians from primitive gaussians. Gaussians from the same shell share the same exponent, for instance, orbitals $2s$ and $2p$ share the same shell because, whilst $1s$ is in another shell (LEWARS, 2016).

As examples of GTO basis sets and also approaching the one used in this work, it’s possible to cite the split valence double zeta basis set, like 3-21G. In this base the valence is split in two parts, an inner and an outer shell (thus the naming “split valence”) duplicating the amount of basis function (thus, “double zeta”). To represent the inner shell two gaussians are used, on the other hand, for the outer shell only one is used (this is the reason for “21” in the basis set name). For every other orbital that is not a valence one, named core, three gaussians are used to build the basis function (hence the “3”) (JENSEN, 2017; LEWARS, 2016).

Finally, it is possible to enhance the split valence double zeta basis set by adding polarization and/or diffusion functions. Polarization functions are used to account for the electron polarization effect (being spread in a specific direction), in a basis set it is donated as $*/(d)$ or $*/(d,p)$ in the end of its name, to indicate polarization on heavy atoms or heavy atoms and hydrogens. The diffusion function is added to a basis set to make the gaussian fall

off slowly as it gets further away from its peak. This diffusion of the gaussian allows to better measure electronic interaction in electric charged molecules. Similarly to polarization, diffusion function is represented by + or ++ just before the “G” in the basis name, to indicate the diffusion gaussians for heavy atoms or heavy atoms and hydrogens (LEWARS, 2016).

APPENDIX D. HISTORICAL DEVELOPMENT OF THE CONDENSED-TO-ATOMS FUKUI INDEX

Reactivity analysis of molecules and atoms are indeed a topic of interest, given it allows comprehending and predicting chemical interactions and reactions. In this sense, there was a historical search for parameters that offered such information. One of the first descriptors defined was the global reactivity (global hardness (η) and global softness(S)), by Parr and Pearson in 1983 (PARR; PEARSON, 1983).

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{\nu(\mathbf{r})} = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_{\nu(\mathbf{r})} \quad (\text{D.1})$$

$$S = \frac{1}{2\eta} = \left(\frac{\partial N}{\partial \mu} \right)_{\nu(\mathbf{r})} \quad (\text{D.2})$$

where E is the system's total energy and N is the total number of electrons; $\nu(\mathbf{r})$ is the external electric potential, represented by nuclei positioning, and therefore considered constant. Finally, μ is the chemical potential, identified as the opposite of electronegativity, as defined by Iczkowski and Margrave in 1961 (ICZKOWSKI; MARGRAVE, 1961). In a finite approach, hardness and global softness can be rewritten as:

$$\eta = \frac{IP - EA}{2} \quad (\text{D.3})$$

$$S = \frac{1}{IP - EA} \quad (\text{D.4})$$

where, IP and EA are acronyms for ionizing potential and electron affinity of a molecule, respectively. And still in a finite approach, they can be written as:

$$IP = E(N - 1) - E(N) \quad (\text{D.5})$$

$$EA = E(N) - E(N + 1) \quad (\text{D.6})$$

Parr and Yang works with these definitions of global hardness and softness to offer a derivation, or rationalizations at least, of Pearson's hard-soft acid and bases (HSAB) principle that states: Both in their thermodynamic and kinetic properties, hard acids prefer hard bases, and soft acids prefer soft bases (PARR; YANG, 1994; PEARSON, 1963).

Equation (C.1) shows a partial derivative of the chemical potential, another one is possible, derivative in function of the external potential, also written as partial derivative of the electronic density in relation to the total number of electron (with constant ν):

$$f(\mathbf{r}) = \left[\frac{\delta\mu}{\delta\nu(\mathbf{r})} \right]_N = \left[\frac{\delta\rho(\mathbf{r})}{\delta N} \right]_\nu \quad (\text{D.7})$$

This is the Fukui function of the system (PARR; PEARSON, 1983; PARR; YANG, 1994). Its physical meaning comes from the first part of the equation (C.7), measuring how sensitive the system's chemical potential is to an external perturbation at a particular point (thus the $\mathbf{r}$ dependence). The second part works with the electron density of an atom or molecule in their valence region. An important fact discussed by Parr and Yang is that a derivative in N has, in general, a value when approaching from the right, one when approaching from the left and an average value (PARR; YANG, 1994). These three different values birth three indexes

$$f^+(\mathbf{r}) = \left[\frac{\delta\rho(\mathbf{r})}{\delta N} \right]_\nu^+ \quad (\text{D.8})$$

$$f^-(\mathbf{r}) = \left[\frac{\delta\rho(\mathbf{r})}{\delta N} \right]_\nu^- \quad (\text{D.9})$$

$$f^0(\mathbf{r}) = \frac{1}{2} [f^+(\mathbf{r}) + f^-(\mathbf{r})] \quad (\text{D.10})$$

The “+” represents the derivative as N goes to $N+\delta$, whilst “-” represents the derivative when $N-\delta$ goes to N , therefore “0” stands for the average value.

One interpretation is that f^+ and f^- are approximations for LUMO and HOMO electronic densities, respectively. Also that they measure reactivity toward a nucleophilic reagent (f^+), an electrophilic reagent (f^-) or a free radical (f^0) (FUKUI; YONEZAWA; SHINGU, 1952; PARR; YANG, 1994).

The previous equations for the Fukui function considers infinitesimal electron changes, however it is desirable to observe and study situations where $\delta=1$, that is, a whole electron is added or removed. In this sense, Yang and Mortier (YANG; MORTIER, 1986) proposed an approximation considering finite changes to electronic population as well as its effect in each atom, that was the CAFI, and the equations are the following:

$$f_k^+ = p_k(N_0 + 1) - p_k(N_0) \quad (\text{D.11})$$

$$f_k^- = p_k(N_0) - p_k(N_0 - 1) \quad (\text{D.12})$$

$$f_k^0 = \frac{1}{2} [p_k(N_0 + 1) - p_k(N_0 - 1)] \quad (\text{D.13})$$

As explained in the main text, k represents the k -th atom of the system whilst p_k represents its electronic population, where N_0 is the total number of electrons in a neutral situation, therefore, N_0+1 is an anionic and N_0-1 is a cationic state. The interpretation for each index remains the same from the Fukui function.

For the most part, CAFI is relatively simple to calculate, it requires the measurement to be made before relaxation, that is, after the charge is changed there is no geometry optimization process. The big challenge to overcome is to decide how to calculate the p of each atom, in other words, how the charge is partitioned in the molecule. By default, Gaussian 16 uses Mulliken population analysis (MULLIKEN, 1955), which can bring undesirable negative values to CAFI. On the other hand, one may change the partitioning used by Gaussian 16 to Hirshfeld partitioning (HIRSHFELD, 1977), which is regarded as the best and most reliable option for this application, as shown by Roy and his collaborators (ROY; PAL; HIRAO, 1999). As Hirshfeld partitioning is the one used in this work, it is discussed in greater details in Appendix E.

APPENDIX E. HIRSHFELD CHARGE PARTITIONING

The choice of a great and reliable charge partitioning method is vital for CAFI studies, given the reliability of its results are dependent on the method of choice. As previously mentioned (Appendix D), some methods can lead to negative results, which are of very complicated interpretation and should be avoided (ROY; PAL; HIRAO, 1999). To do so, one should consider using the Hirshfeld partitioning method, also known as the stockholder partitioning. It was defined by Hirshfeld itself in 1977, and considers charges as deformation density ($\rho_d(\mathbf{r})$) (HIRSHFELD, 1977).

This $\rho_d(\mathbf{r})$ is the difference between the molecules charge density and the atomic charge “without relaxation” (which is associated with a promolecule), and is written as:

$$\rho_d(\mathbf{r}) = \rho^{mol}(\mathbf{r}) - \rho^{pro}(\mathbf{r}) = \rho^{mol}(\mathbf{r}) - \sum_{\alpha} \rho_{\alpha}(\mathbf{r} - \mathbf{R}_{\alpha}) \quad (\text{E.1})$$

where the superscripts *mol* and *pro* indicate that said ρ is from the molecule, or promolecule, respectively, in a given site $\mathbf{r}$. On the other hand, $\rho_{\alpha}(\mathbf{r} - \mathbf{R}_{\alpha})$ represents the ground state charge density of a free atom α , positioned at $\mathbf{R}_{\alpha}$. From (E.1) it's possible to understand what is a promolecule, basically a molecule where atoms don't interact with each other and have spherical charge densities.

With that it's possible to define the effective atomic charge q_{α} :

$$q_{\alpha} = - \int \rho_d(\mathbf{r}) w_{\alpha} d^3\mathbf{r} \quad (\text{E.2})$$

where w_{α} is a “sharing function” that measures how many “shares” an atom α has in the promolecule density at a position $\mathbf{r}$. This sharing function is defined as:

$$w_{\alpha} = \rho_{\alpha}(\mathbf{r} - \mathbf{R}_{\alpha}) \left[\sum_{\beta} \rho_{\beta}(\mathbf{r} - \mathbf{R}_{\beta}) \right]^{-1} \quad (\text{E.3})$$

In short, a promolecule is built based on atoms' well defined charge densities, then the real charge density at each point is divided among the atoms proportionally to each atom's contribution to the promolecule's charge density. It works like partners in a stockholders company, each atom is going to take gains or losses proportional to how much they've “invested” (how important they are in the promolecule).

APPENDIX F. BASIC ASPECTS OF TIME-DEPENDENT DFT

In the 80s DFT was already a pretty valuable tool for many body problems, for atomic, molecular, solid-state or even nuclear physics. However there was still interest to compute problems related to the electronic excited state (EES) that are time-dependent (TD) phenomena, such as atomic and nuclear scattering, photoabsorption, etc (RUNGE; GROSS, 1984). However, by that time, there was no equivalent to HK theorems (see Appendix A), until Runge and Gross formalized it in 1984 (JACQUEMIN; MENNUCCI; ADAMO, 2011; RUNGE; GROSS, 1984).

In this paper, Runge and Gross proposed four theorems, and offered proof for each one of them in a mathematical approach. The authors did it in such a way that this TD solution can be reduced to the common Hohenberg-Kohn-Sham theory in the limit of stationary ground states. From this work, theorems 2, 3 and 4 allow for three different practical schemes to calculate the density, however the fourth one is the most attractive one since it produces a quantum mechanical structure in the most natural way. This theorem says that the exact TD density of the system can be computed from:

$$n(\mathbf{r} t) = \sum \phi_j^*(\mathbf{r} t) \phi_j(\mathbf{r} t) \quad (\text{F.1})$$

where $\phi_j(\mathbf{r} t)$ are single-particle orbitals and fulfill the TD-SE:

$$(i\partial/\partial t + \frac{1}{2}\nabla^2)\phi_j(\mathbf{r} t) = v_{eff}[\mathbf{r} t; n(\mathbf{r} t)]\phi_j(\mathbf{r} t) \quad (\text{F.2})$$

where v_{eff} is an effective one-particle potential given by:

$$v_{eff}[\mathbf{r} t, n(\mathbf{r} t)] = v(\mathbf{r} t) + \int d^3r' n(\mathbf{r}' t) w(\mathbf{r}, \mathbf{r}') + \delta A_{XC}/\delta n(\mathbf{r} t) \quad (\text{F.3})$$

where v is the single-particle potential, w is the electron-electron repulsion and A_{XC} is the XC part of the action integral.

It must be highlighted that this so-called density in Runge and Gross theorems is the probability (normalized to N particles) of finding any one electron of a given spin at a position $\mathbf{r}$. As mentioned, theorems 2, 3 and 4 provide ways to calculate the density, however the core of the theory is the first theorem, which proves an one-to-one correspondence between the external potential and the density. This means if only the TD density of a system is known, then this identifies the external potential, which in turns completely identifies the Hamiltonian. The TD SE can be solved and all properties obtained (MARQUES et al., 2012, 2012).

APPENDIX G. ELECTROPHILICITY, DAM, AND LEDAP

The magnitude called electrophilicity index, often labeled as ω , can be defined as an index to measure the energy change of an electrophile material when it gets saturated with electrons. Mathematically, it can be expressed in terms of the chemical potential (μ) and chemical hardness (η) as (GÁZQUEZ; CEDILLO; VELA, 2007):

$$\omega = \frac{\mu^2}{2\eta} \quad (\text{G.1})$$

And by considering finite difference approximation for μ and η , we can write the electrophilicity in terms of the ionizing potential (IP) and the electron affinity (EA):

$$\omega \approx \frac{(IP + EA)^2}{8(IP - EA)} \quad (\text{G.2})$$

This is a valuable approximation given that these magnitudes can be easily calculated by total energy differences (equations D.5 and D.6), requiring low computational power. However, one might not forget that IP and EA ultimately came from energy derivatives considering an electron number variation. In the paper by Gázquez, Cedillo, and Vela, they point out the discontinuity in the first and second derivatives when evaluated from the left or from the right, which ultimately leads to two different indexes (GÁZQUEZ; CEDILLO; VELA, 2007), in a similar fashion as the Fukui function by Parr and Yang (PARR; YANG, 1994). The indexes, considering the discontinuity and finite approach are:

$$\omega^+ \equiv \frac{(\mu^+)^2}{2\eta} \approx \frac{(IP + 3EA)^2}{16(IP - EA)} \quad (\text{G.3})$$

$$\omega^- \equiv \frac{(\mu^-)^2}{2\eta} \approx \frac{(3IP + EA)^2}{16(IP - EA)} \quad (\text{G.4})$$

These are the global electron accepting (ω^-) and electron donating powers (ω^+), meaning they are a single measure for the whole molecule, similar to the softness S in ch.2 and Appendix D.

Considering these powers, it is possible to compare different materials. One way to do it was proposed by Martínez *et al* (MARTÍNEZ et al., 2008). To compare the acceptance capabilities of a given material, the authors proposed an electron acceptance index (R_a) which compares the material's electron accepting power to fluor's. And then, proposed an electron

donation index (R_d), comparing the material's electron donating power to sodium's power. Mathematically:

$$R_a = \frac{\omega^+}{\omega_F^+} \quad (\text{G.5})$$

$$R_d = \frac{\omega^-}{\omega_N^-} \quad (\text{G.6})$$

When these indexes are around one, it means the material is as good an electron acceptor (donor) as the F (Na) atom. However, bigger values indicate better electron acceptors and worse electron donors. The opposite is true, smaller values are better for donation and worse for acceptance. Plotting R_d vs R_a provides a donor acceptor map, DAM.

This is an analysis focused on the global aspect of the material, to understand how good of an electron acceptor/donor it is. However, a local approach is possible. Gázquez and his collaborators proposed a local version of the electron accepting/donating power to study how these powers vary at each different region of a molecule. To do so, the authors derived a local function $\omega^n(\mathbf{r})$, that can be written as a multiplication between the global power ω^n by the Fukui function $f^n(\mathbf{r})$ ($n=+$ or $-$, for electron donation or acceptance, respectively) (GÁZQUEZ; CEDILLO; VELA, 2007). However, it is possible to use the condensed-to-atoms approach for the Fukui function, which gives the condensed-to-atoms Fukui indexes (CAFI - See Appendix D) an approximation considering finite changes to electronic population, as well as its effect in each atom. Thus, given us the local electron donating and accepting powers (LEDAP), for each site (atom) as:

$$\omega_k^+ = \omega^+ f_k^+ \quad (\text{G.7})$$

$$\omega_k^- = \omega^- f_k^- \quad (\text{G.8})$$

This, and the function, approaches still have a problem at the ω_k^- (or $\omega^-(\mathbf{r})$). As seen for DAM, bigger ω^- means worse electron donation, while bigger f_k^- means a higher chance to interact with an electrophilic agent (donate electrons). To make these magnitudes operate well together, and have an smooth and consistent graphical representation (as in CAFI results), we decided to use a modified local electron donating power, defined as:

$$\omega_k^{-*} = \frac{f_k^-}{\omega^-} \quad (\text{G.9})$$

Considering this modification, the LEDAP results can be plotted over the atoms, just like CAFI. If plotted directly, both will be the same since it is normalized per molecule. Therefore, by adjusting the routine to normalize to the highest values of ω_k^+ and ω_k^- among

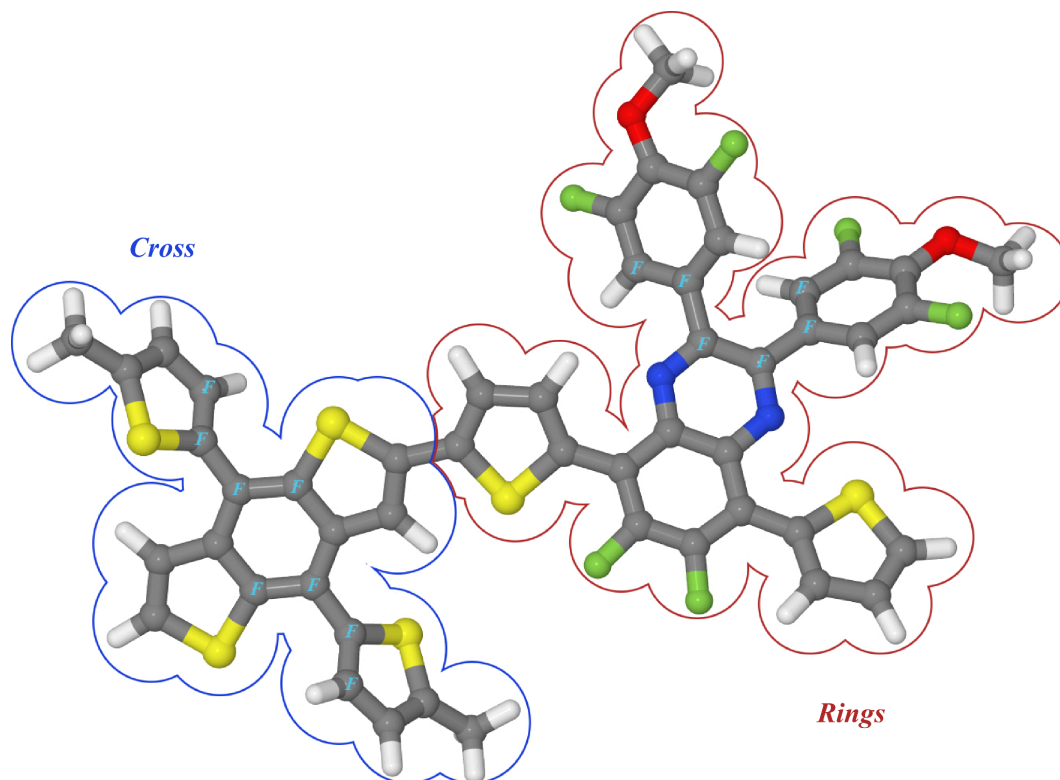
the compared materials, it's possible to visualize the difference in electron acceptance/donation between them.

APPENDIX H. BUILDING HFQX-T MONOMER UNIT

The donor polymer HFQx-T has a complex structure with alkyl side chains, internal dihedral angles and rotating rings, that builds to a high level of freedom and a very computational demanding polymer. To mitigate the cost, it is important to reduce the degrees of freedom as much as possible and carefully build a monomer that, when connected to other units, will not require much further calculations. It must be noted that a first monomer was built with the same methods as the ones for PM6 and D18, and from there more studies were made.

The substitution of the long alkyl side chains for methyl was expected anyway, as shown before with Y6's studies. However there are still many things to solve regarding the internal dihedrals and the rings' dihedrals. One important decision to properly build this monomer was to separate it in two, Figure G.1 illustrates this division. Furthermore, for bigger structures some dihedrals need to be frozen, Figure G.1 also illustrates that by marking atoms with the letter F.

Figure H.1. HFQx-T separation in two structures and important dihedrals to be frozen.



Source: Author.

Notice that now there are two structures named Cross and Rings. When separated the broken bond was fixed with a H atom. Then each of them were optimized again, and dihedral scan calculations were performed, considering the marked atoms from Figure G.1. The dihedrals found in the scan were set and the molecules were optimized once again.

For Cross the scan results were pretty direct, however due to its symmetry it can bond to Rings in two ways, producing two different structures, here called V1 and V2 for sake of simplicity.

Rings scan results showed two very similar structures, that after optimization became even more similar. Energetically their difference is way smaller than kT . For simplicity, the lowest total energy structure is chosen.

The combination Cross-Rings produced V1 and V2, as mentioned. V1 is the one in Figure G.1, V2 has the selected dihedrals rotated 180° (S atom behind the molecular plane for the upper thiophene and in front of the molecular plane for the lower). This subtle difference also resulted in a very subtle E_T difference after optimization, 0.002 eV. Their FMO energies were also similar. Choosing either V1 or V2 is acceptable, for no particular reason V1 was kept for building bigger structures.

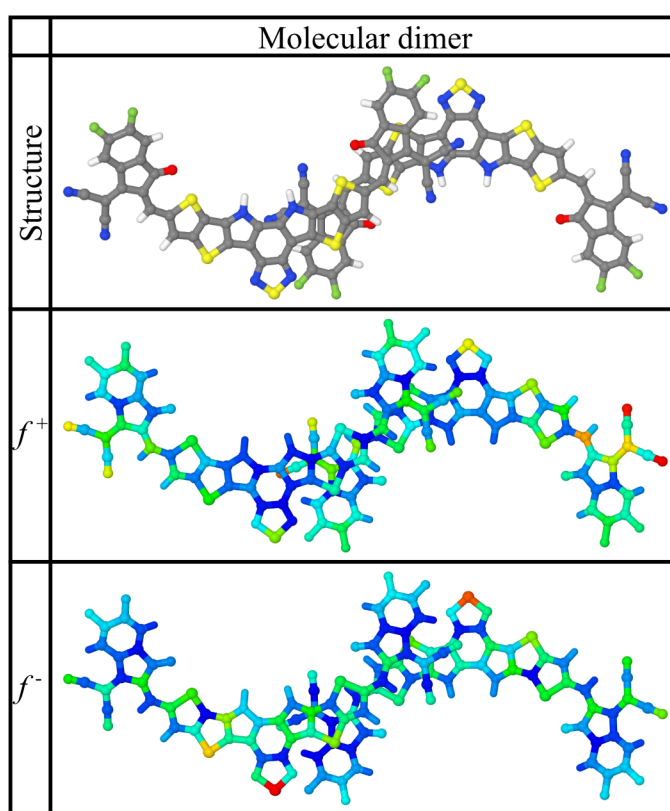
At this moment, finally a good monomer of HFQx-T is built, which was then freely optimized to allow all dihedrals to relax. This relaxation was subtle, around 1° for each dihedral. From now on, optimizations of HFQx-T will have the highlighted dihedrals (Figure G.1) frozen during optimization to minimize computational cost.

APPENDIX I. CAFI APPLIED TO Y6 DIMERS

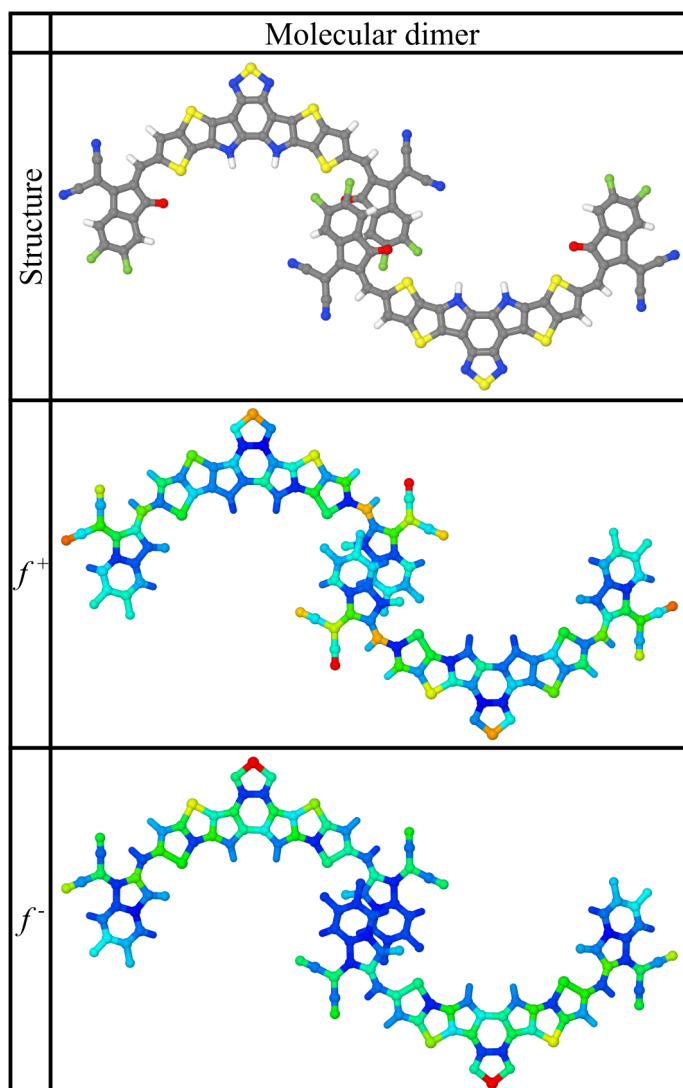
In this work, the reactivity descriptor CAFI found single-molecule systems' electron donation and reception sites. Conversely, CTFI found charge transfer sites in dimeric systems. At last, here, the results of CAFI studies on dimeric systems are presented.

The results are the dimeric systems used for the CTFI study combined with the regular CAFI calculation method. Figures I.1 to I.4 present these results for dimers S1, S2, Y, and U.

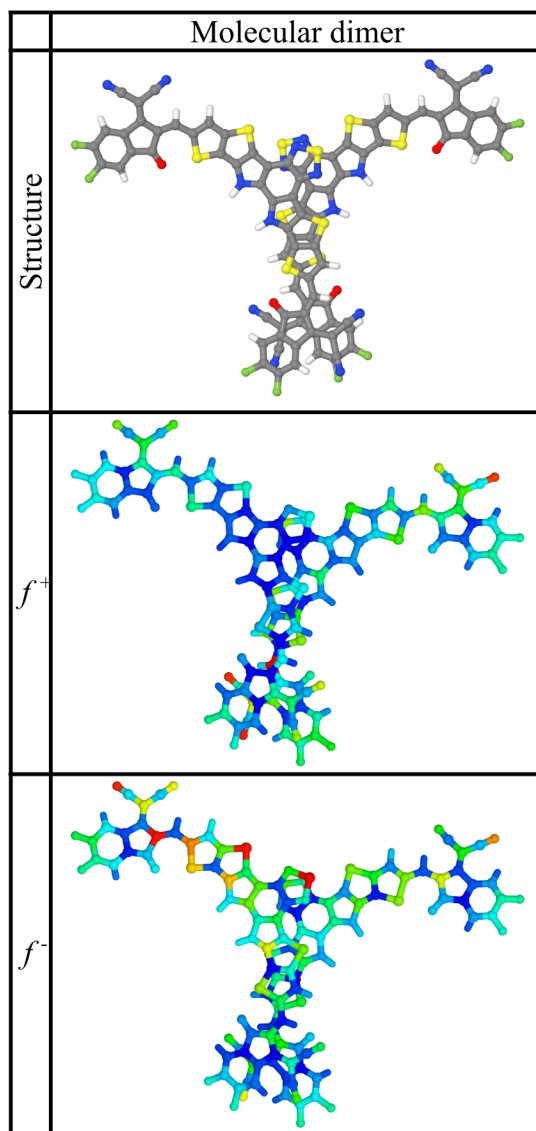
Figure I.1. Dimeric CAFI for dimer-S1.



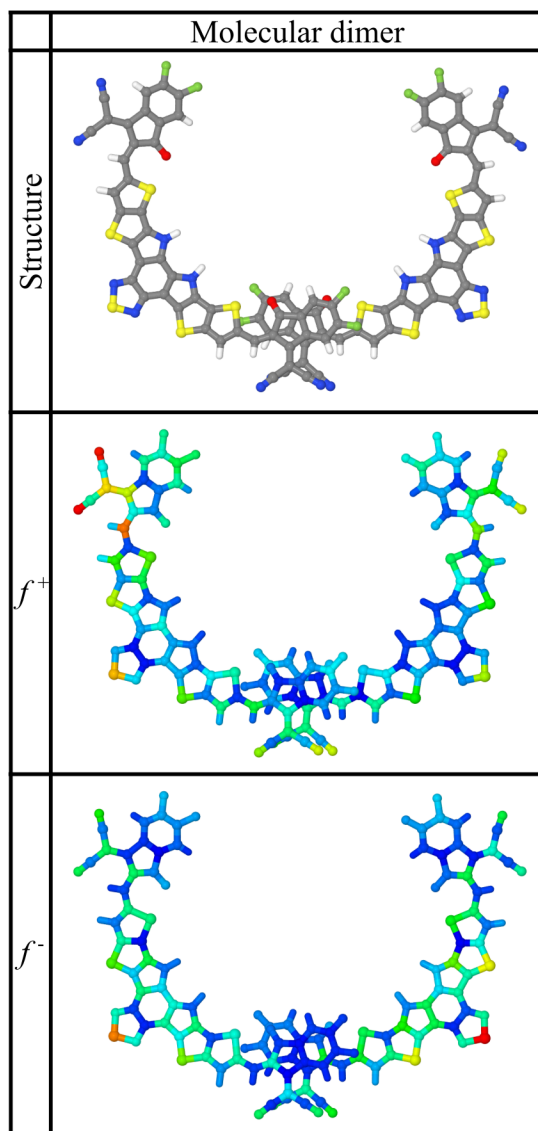
Source: Author.

Figure I.2. Dimeric CAFI for dimer-S2.

Source: Author.

Figure I.3. Dimeric CAFI for dimer-Y.

Source: Author.

Figure I.4. Dimeric CAFI for dimer-U.

Source: Author.

In brief, the Y6 single-molecule CAFI showed strong reactive f^+ sites for S_c and N_D atoms. For f^- the only relevant reactive site was also S_c . Moreover, dimeric CAFI results show these same reactive sites, but not always in both Y6s nor necessarily respecting which sites are from which index (f^+ or f^-).

In particular, dimer-S2 shows the closest resemblance to the single-molecule result. The same sites are reactive, aside from the expected edge effects. Not too far from this result, dimer-S1 and -U are close to a simple stack of individual results. What might explain these results is the simplicity of the dimers, where the most reactive sites of Y6 are not stacked.

This explanation is consistent with the dimer-Y result. This dimer has the most intricate stacking, with multiple regions of interest interacting. Unsurprisingly, it presents the furthest results from the single-molecule, with highly reactive N atoms at the f - index.

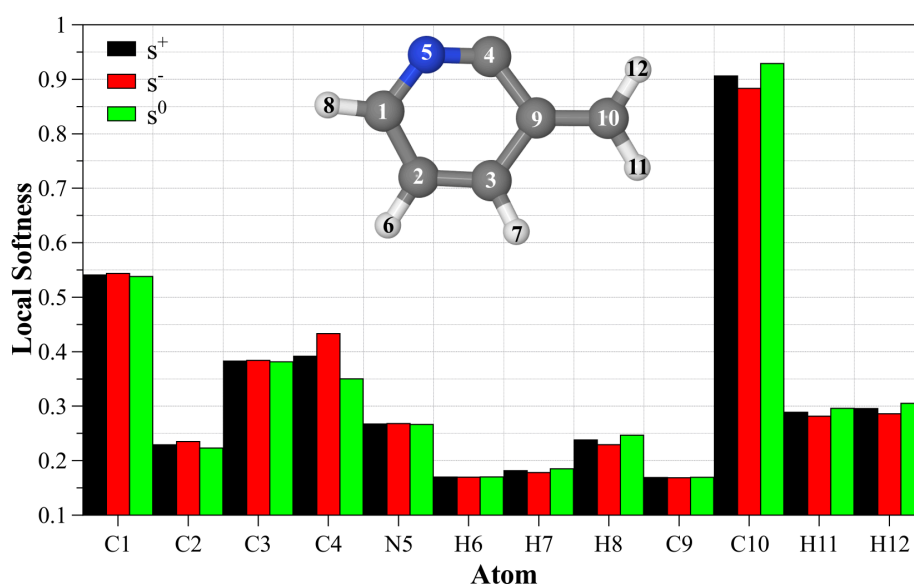
All the results presented offer minimal insights on the charge transfer process and hopping pathways. It only serves to reinforce the importance and quality of an approach such as CTFI, where proper calculations are made to obtain CT information.

APPENDIX J. CHAPTER 2 SUPPLEMENTARY RESULTS

In this appendix supplementary data from chapter 2 are displayed, such as open-shell structures, and additional calculated molecules.

J.1. Aza-H (OS)

Figure J.1. Numbered structure for Aza-H (OS) and graph for local softness results.



Source: Author.

Table J.1. ΔH , ΔE_T , S , LS and Q values for Aza-H (OS) atoms.

S	4.0607	ΔE_T (kcal/mol)	21.8	ΔH	45.8	Atom	Q
	s^+	s^-		s^0			
C10	0.9289	C10	0.8833	C10	0.9061	C1	0.0656
C1	0.5380	C1	0.5436	C1	0.5408	C2	-0.1873
C3	0.3815	C4	0.4332	C4	0.3917	C3	0.0165
C4	0.3501	C3	0.3840	C3	0.3827	C4	0.1411
H12	0.3052	H12	0.2860	H12	0.2956	N5	-0.2637
H11	0.2960	H11	0.2816	H11	0.2888	H6	0.1051
N5	0.2665	N5	0.2681	N5	0.2673	H7	0.1022
H8	0.2467	C2	0.2351	H8	0.2380	H8	0.1245
C2	0.2232	H8	0.2293	C2	0.2291	C9	-0.1842
H7	0.1850	H7	0.1782	H7	0.1816	C10	-0.1528

S	4.0607	ΔE_T(kcal/mol)	21.8	ΔH	45.8	Atom	Q
	s^+	s^-		s^0			
H6	0.1701	H6	0.1697	H6	0.1699	H11	0.1108
C9	0.1695	C9	0.1686	C9	0.16903	H12	0.1221

Source: Author.

Table J.2. Compiled results for Aza-H (OS) probable interactions.

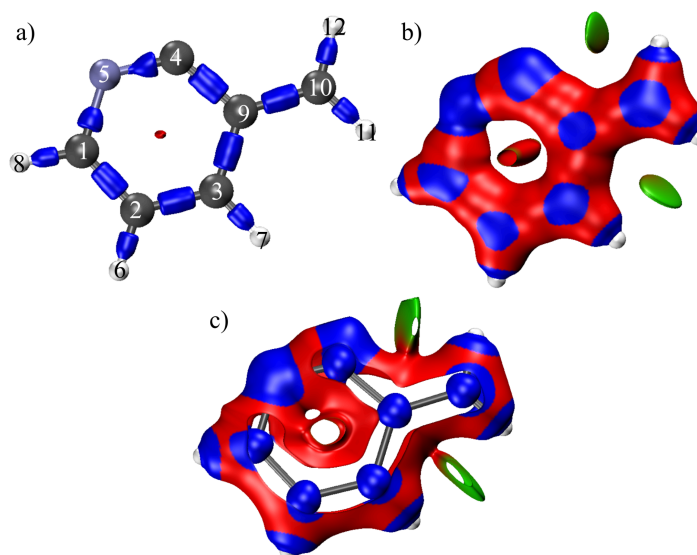
Atoms	Int. Type	Δs	Σs	ΔQ	$\frac{\Delta s}{\Sigma s}$	$\frac{\Delta s}{\Delta Q * \Sigma s}$
C4/C10	s_4^+/s_{10}^-	0.5559	1.3621	0.2939	0.4081	1.3886
	s_4^-/s_{10}^+	0.4957	1.2334		0.4019	1.3675
	s_4^0/s_{10}^0	0.5144	1.2977		0.3963	1.3487
C3/C10	s_3^+/s_{10}^-	0.5018	1.2647	0.1693	0.3968	2.3436
	s_3^-/s_{10}^+	0.5449	1.3129		0.4150	2.4513
	s_3^0/s_{10}^0	0.5233	1.2888		0.4060	2.3983
C3/C4	s_3^+/s_4^-	0.0517	0.7655	*	0.0675	*
	s_3^-/s_4^+	0.0339	0.7341		0.0462	*
	s_3^0/s_4^0	0.0089	0.7744		0.0115	*
C1/C3	s_1^+/s_3^-	0.1540	0.9220	*	0.1670	*
	s_1^-/s_3^+	0.1621	0.9251		0.1752	*
	s_1^0/s_3^0	0.1581	0.9235		0.1712	*
C1/C4	s_1^+/s_4^-	0.1048	0.9712	*	0.1079	*
	s_1^-/s_4^+	0.1935	0.8937		0.2165	*
	s_1^0/s_4^0	0.1492	0.9325		0.1600	*

*atoms with same sign charges

Source: Author.

In general the results coming from CS systems are well aligned with the OS ones. What seems as the most deviant result is the C3/C4 interaction, which has the lowest set of $\Delta s/\Sigma s$, for CTR and RR. This is an intriguing interaction that leads Aza-H back to 1-azafulvenallene. The caveat here is that, in relation to in-ring/out-ring atoms interaction, it is likely overestimated, which means C4/C10 and C3/C10 might be more relevant than what the results ($\Delta s/\Sigma s$) indicate. Complementary to this discussion, Figure J.2 brings the IRI results for Aza-H (OS), considering 3 different isovalues.

Figure J.2. Aza-H (OS)'s IRI result considering isovalue of a) 0.9, b) 2.1 and c) 2.5



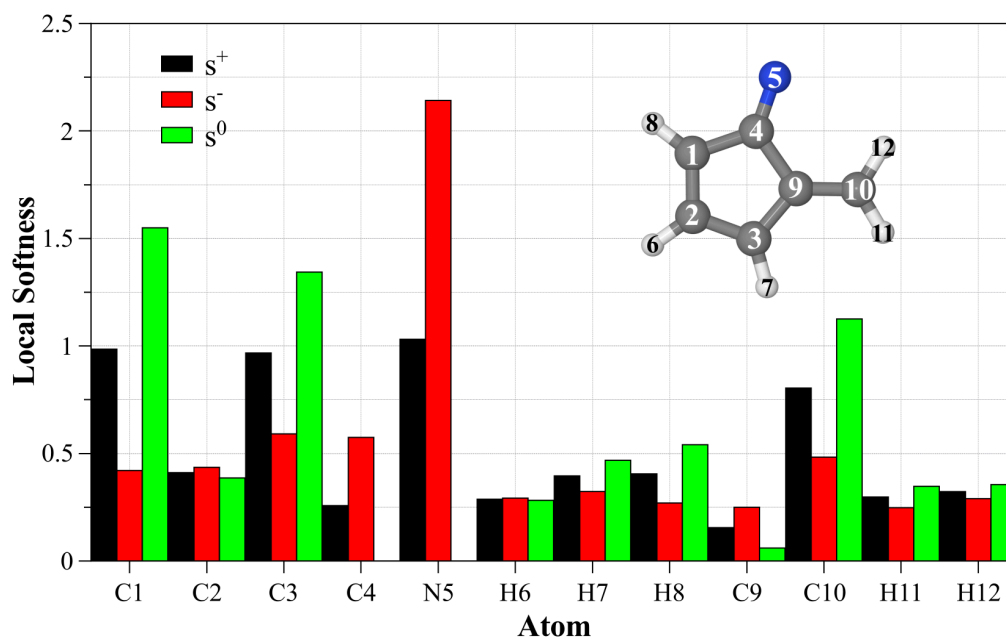
Source: Author.

Compared to its CS structure, the main differences are the bigger gap in the ring inner isosurface (easier C1-C4 interaction), and the bigger VdW interaction surface between C4-C10.

In general, OS reinforces the paths C1-C4 (Aza-L), C3-C10 (Aza-O), and C4-C10 (Aza-W4). It also brings the possibility of backwards reactions, with C3-C4 interacting back to 1-azafulvenallene.

J.2. Aza-N (OS)

Another OS structure mentioned in the main text is Aza-N, whose LS results are presented here by Figure J.3 and Table J.3.

Figure J.3. Numbered structure for Aza-N (OS) and graph for local softness results.

Source: Author.

Table J.3. ΔH , ΔE_T , S , LS and Q values for Aza-N (OS) atoms.

S	4.1677	$\Delta E_T(\text{kcal/mol})$		24.0	ΔH	3.5	Atom	Q
	s^+	s^-			s^0			
C1	1.5497	N5	2.1419	N5	1.0312		C1	-0.0929
C3	1.3437	C3	0.5912	C1	0.9852		C2	-0.0430
C10	1.1257	C4	0.5749	C3	0.9674		C3	0.0443
H8	0.5407	C10	0.4830	C10	0.8043		C4	-0.1051
H7	0.4683	C2	0.4356	C2	0.4109		C5	-0.0195
C2	0.3862	C1	0.4208	H8	0.4052		N6	-0.3376
H12	0.3553	H7	0.3231	H7	0.3957		C7	-0.0596
H11	0.3473	H6	0.2924	H12	0.3226		H8	0.1183
H6	0.2821	H12	0.2899	H11	0.2976		H9	0.1166
C9	0.0604	H8	0.2697	H6	0.2873		H10	0.1184
C4	0	C9	0.2497	C4	0.2575		H11	0.1388

N5	0	H11	0.2478	C9	0.1551	H12	0.1213
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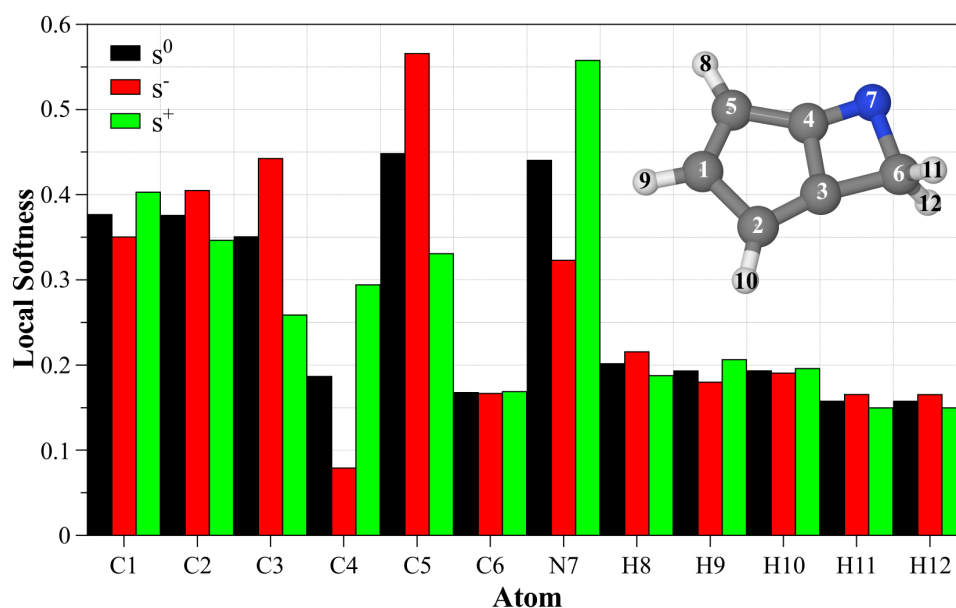
Source: Author.

The results for OS calculations are extremely similar to the CS. Atom N5 stands out as the softest s^- by a large margin, it also stands out even compared to the softest s^+ atoms (C1, C3, C10), which are already three times larger than the rest of the s^+ . These results bring nothing new, all the interactions found are the same, there is no reason to analyse it further.

J.3. Aza-N4

As stated in the main text, there are a few alternative routes found in the pathway between 1-azafulvenallene and phenylnitrene. One of these routes is the molecule Aza-N, which has CS and OS structures. Here the results for its OS structure are presented and discussed. Figure J.4 and Tables J.4 bring the results from LS calculations.

Figure J.4. Numbered structure for Aza-N4 and graph for local softness results.



Source: Author.

Table J.4. ΔH , ΔE_T , S , LS and Q values for Aza-N4 atoms.

S	3.2481	$\Delta E_T(\text{kcal/mol})$	*	ΔH	*	Atom	Q
	s^+	s^-		s^0			
N7	0.5576	C5	0.5657	C5	0.4482	C1	-0.0954
C1	0.4029	C3	0.4424	N7	0.4403	C2	-0.1212

C2	0.3464	C2	0.4048	C1	0.3766	C3	-0.1272
C5	0.3307	C1	0.3503	C2	0.3756	C4	0.1684
C4	0.2940	N7	0.3229	C3	0.3505	C5	-0.0830
C3	0.2587	H8	0.2155	H8	0.2015	C6	-0.0596
H9	0.2062	H10	0.1905	H10	0.1932	N7	-0.2632
H10	0.1958	H9	0.1798	H9	0.1930	H8	0.1047
H8	0.1875	C6	0.1666	C4	0.1866	H9	0.1110
C6	0.1687	H11	0.1653	C6	0.1677	H10	0.1002
H12	0.1497	H12	0.1652	H11	0.1575	H11	0.1327
H11	0.1496	C4	0.0790	H12	0.1574	H12	0.1326

* data not available

Source: Author.

From the graph, notice that C5, N7, and C3 are the softest atoms in the molecule. C1 and C2 come next but are too far from any interactable atom other than in-ring atoms. There are actually just two interactions of interest, C5/N7, and C3/N7. The first is another occurrence of a backward path, back to Aza-N. This pathway back might not be as easy to achieve (despite LS) due to the distance and the C6-N7 bond. The second is a bit more interesting as it might lead to the incorporation of N in the ring. The resulting structure is not present among the one found before, not even in Figure 2.15, which sets it as a target for further studies. Table J.5 presents the compiled results and $\Delta s/\Sigma s$ parameters. Interaction between atoms with different signed charges is absent, so ΔQ and Eq. (2.8) are omitted.

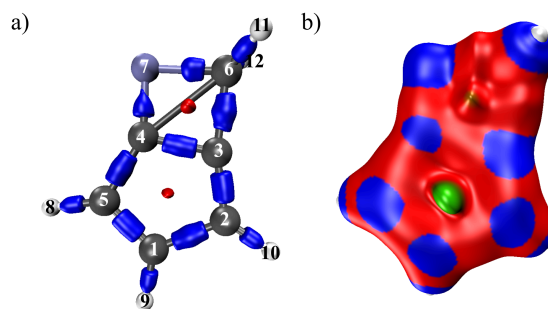
Table J.5. Compiled results for Aza-N4 probable interactions.

Atoms	Int. Type	Δs	Σs	$\frac{\Delta s}{\Sigma s}$
C5/N7	s_5^-/s_7^+	0.0081	1.1233	0.0072
	s_5^0/s_7^0	0.0079	0.8885	0.0089
C3/N7	s_3^-/s_7^+	0.1152	1.0000	0.1152

Source: Author.

The results for C5/N7 reached a new lowest value. The only way for it not to happen would be the mentioned distance barrier and C6 bond. To verify these options through another method, Figure J.5 brings the IRI results for a 0.9 and 2.5 isosurface.

Figure J.5. Aza-N4's IRI result considering isovalue of a) 0.9, and b) 2.5

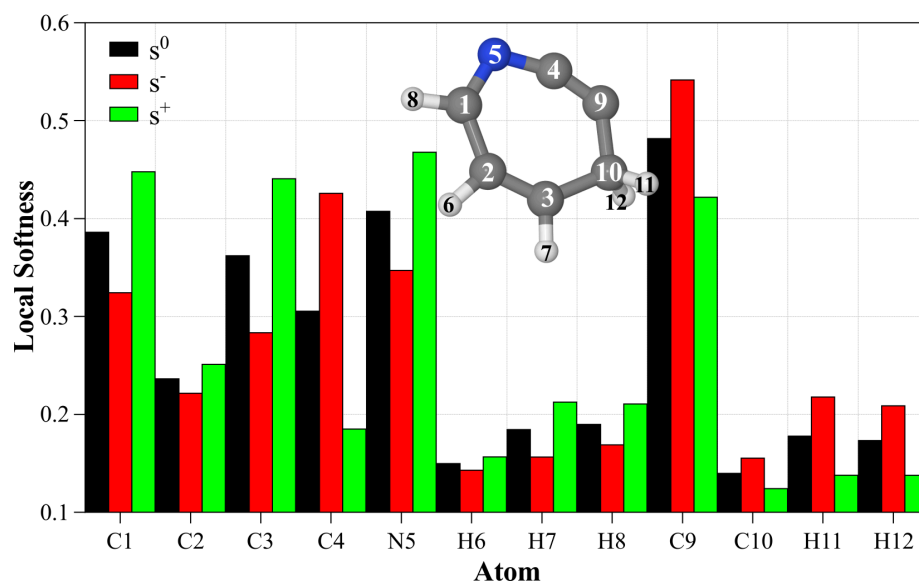


Source: Author.

From (a), it's made clear that C3/N7 would be quite energetically expensive, given the presence of a big steric effect bubble, bigger than the one in the main ring. Also it is worth noting that the C6-N7 and C4-N7 bonds do not have attractive interactions such as the ones in other bonds, suggesting a weaker or more unstable bonding. Notice, however, that the latter is still better than the first. Moreover, at (b) it is possible to note a repulsive bulge between C6 and N7. Considering this IRI analysis, the only path to Aza-N4 is to go backwards, to Aza-N (which itself has a favorable backwards path to Aza-L). Molecules such as Aza-N and -N4 can be seen as examples of inefficiency in the process of turning 1-azafulvenallene into phenylnitrene, maybe becoming byproducts or simply delaying the reaction to the final product.

J.4. AZA-W5 AND AZA-W3

The Aza-W4, an alternative path from Aza-H, led to a follow up in Aza-W5, a seven-atom ring molecule where C10 still has both H atoms, while C9 has none. Such H adjustments are chemically expected, however cannot be predicted by LS. Therefore, this path has to be done exclusively over IRC calculations. Regardless of this inaccessible information, Figure J.6 and Table J.6 bring the LS results for a brief analysis.

Figure J.6. Numbered structure for Aza-W5 and graph for local softness results.**Table J.6.** ΔH , ΔE_T , S , LS and Q values for Aza-W5 atoms.

S	3.1934	$\Delta E_T(\text{kcal/mol})$	40.5	ΔH	3.5	Atom	Q
	s^+	s^-		s^0			
N5	0.4677	C9	0.5416	C9	0.4817	C1	0.0385
C1	0.4478	C4	0.4258	N5	0.4074	C2	-0.1472
C3	0.4407	N5	0.3470	C1	0.3860	C3	-0.1012
C9	0.4218	C1	0.3242	C3	0.3620	C4	0.0231
C2	0.2511	C3	0.2834	C4	0.3054	C5	-0.2634
H7	0.2125	C2	0.2215	C2	0.2363	C6	0.1091
H8	0.2106	H11	0.2177	H8	0.1897	N7	0.1128
C4	0.1850	H12	0.2087	H7	0.1845	H8	0.1267
H6	0.1565	H8	0.1689	H11	0.1778	H9	-0.0257
H11	0.1378	H7	0.1564	H12	0.1732	H10	-0.1505
H12	0.1378	C10	0.1553	H6	0.1497	H11	0.1388
C10	0.1242	H6	0.1429	C10	0.1397	H12	0.1388

Source: Author.

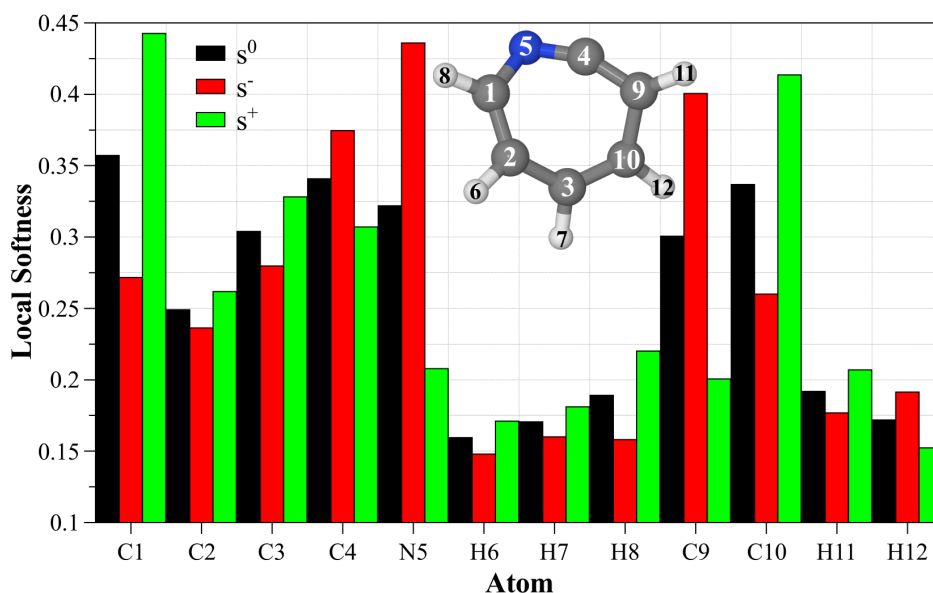
The softest atoms of Aza-W5 are C1, C3, C4, N5, C9. A good property to notice is a balanced LS values for s_k^+ and s_k^0 , where the values decrease more smoothly throughout the table, which allows for more options for interaction

For this brief analysis, the most important information is that C1/C4 interaction is very much possible for a CTR. C1 and C4 have the second highest s_k^+ and s_k^- , respectively, losing to N5 and C9. However, it's not a problem given N5 is bonded to C4 and C1, and C9 is also bonded to C4, and too far from C1. The only concern would be a N5/C9 interaction, which has a greater ΔS than C1/C4.

In short, the LS analysis provides a path in C1 and C4 bonding, which leads to a molecule very close to phenylnitrene. The H atom adjustments could be done after this interaction, however it was made before, using IRC calculations.

After moving a H atom from C10 to C9, Aza-W3 is obtained. Figure J.7 and Table J.7 present the LS results.

Figure J.7. Numbered structure for Aza-W3 and graph for local softness results.



Source: Author.

Table J.7. ΔH , ΔE_T , S , LS and Q values for Aza-W3 atoms.

S	3.0931	$\Delta E_T(\text{kcal/mol})$		12.6	ΔH 60.7	Atom	Q
	s^+	s^-			s^0		
C1	0.4426	N5	0.4359	C1	0.3571	C1	0.0058
C10	0.4136	C9	0.4005	C4	0.3408	C2	-0.1379
C3	0.3281	C4	0.3745	C10	0.3368	C3	-0.0920
C4	0.3071	C3	0.2797	N5	0.3219	C4	0.1082
C2	0.2618	C1	0.2717	C3	0.3039	N5	-0.2510

H8	0.2201	C10	0.2600	C9	0.3006	H6	0.1124
N5	0.2078	C2	0.2363	C2	0.2491	H7	0.1095
H11	0.2069	H12	0.1914	H11	0.1919	H8	0.1186
C9	0.2006	H11	0.1768	H8	0.1891	C9	-0.1220
H7	0.1811	H7	0.1600	H12	0.1719	C10	-0.0862
H6	0.1710	H8	0.1581	H7	0.1705	H11	0.1105
H12	0.1523	H6	0.1479	H6	0.1595	H12	0.1241

Source: Author.

For Aza-W3, a variety of atoms presented high softness, and as for the Aza-W5, and -W4, a lot of these atoms are already bonded. Nonetheless, there are still new pathways. First, considering RR, C1/C4 is the most promising combination, followed by C4/C10. The first interaction leads to phenylnitrene, while the second might leads to an Aza-M equivalent, which can also get to the targeted molecule according to C. Wentrup and M. S. Mirzaei (MIRZAEI; WENTRUP, 2023).

Considering CTR, C1/C4 interaction shows up once more, as well as the C4/C10. Some of the other combinations involve atoms that are too far to be considered, and others have very different LS values, such as C1/C3. Table J.8. presents the compiled results and $\Delta s/\Sigma s$ parameters.

Table J.8. Compiled results for Aza-W3 probable interactions.

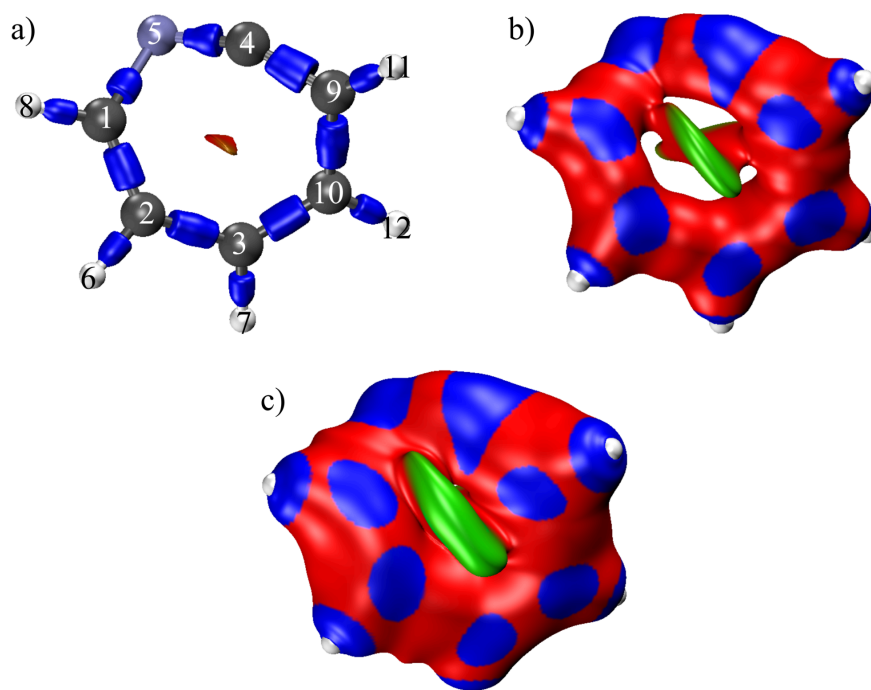
Atoms	Int. Type	Δs	Σs	ΔQ	$\frac{\Delta s}{\Sigma s}$	$\frac{\Delta s}{\Delta Q * \Sigma s}$
C1/C4	s_1^+/s_4^-	0.0681	0.8172	*	0.0833	*
	s_1^-/s_4^+	0.0354	0.5787		0.0612	*
	s_1^0/s_4^0	0.0163	0.6979		0.0234	*
C4/C10	s_4^+/s_{10}^-	0.0470	0.5671	0.1945	0.0829	0.4265
	s_4^-/s_{10}^+	0.0390	0.7881		0.0495	0.2545
	s_4^0/s_{10}^0	0.0040	0.6776		0.0059	0.0304
C1/C3	s_1^+/s_3^-	0.1629	0.7223	0.0977	0.2255	2.3071
	s_1^-/s_3^+	0.0565	0.5998		0.0941	0.9631
	s_1^0/s_3^0	0.0532	0.6611		0.0805	0.8235

*atoms with same sign charges

Source: Author.

For all interactions, RR carried the most likely one. The overall smallest value for $\Delta s/\Sigma s$ was for s_4^0/s_{10}^0 , followed by s_1^0/s_4^0 . However, it is important to highlight that C1/C4 had the softest atoms, thus might have an advantage. Both are relevant results as they go to phenylnitrene. For the CTR, both interactions take the lead, the one to be actually done will depend if Σs has higher importance than Δs , that is, if using the ultimately softest atoms is more important than very similar softness atoms. The interaction C1/C3 presented somewhat competitive CTR results, although the other two are still better. To deeper verify these found interactions, Figure J.8 brings the IRI results.

Figure J.8. Aza-W3's IRI result considering isovalue of a) 0.9, and b) 2.5



Source: Author.

The IRI results do not bring new information, however it answers some questions. First, as C1 bonds with C4, which N5 bond would break? Clearly, C4-N5 has a stronger attraction interaction, therefore it's likely that this bond would not break, and Aza-W3 would indeed go to phenylnitrene. The second question is if is it possible to have a C1/C3 or C4/C10 interaction given the expected steric effect? Yes, indeed it is possible, as it is a bigger ring there is some space with weaker repulsive interactions. However, from (b), there is a repulsive bubble right next to C9, in the way between C4 and C10, thus it seems harder to accomplish

than the C1/C3 interaction. In conclusion, The Aza-W4 path became an alternative pathway to phenylnitrene.

J.5. USING IRI TO EVALUATE THE BONDS

As seen in Chapter 2, the IRI method is able to show the interactive regions using isosurfaces and color maps. There, the main use of IRI was to check for information that the LS method cannot access, such as steric effects, van der Waals interactions and H-bonds. All of that is made using two “cube” files, one with the volumetric surface information, and another with the color map information, made by $sign(\lambda_2)\rho$. When that operation leads to positive (negative) values, it's a repulsive (attractive) region. Thus, one can access the $sign(\lambda_2)\rho$ information of each and every point in a high resolution grid of 10^6 points.

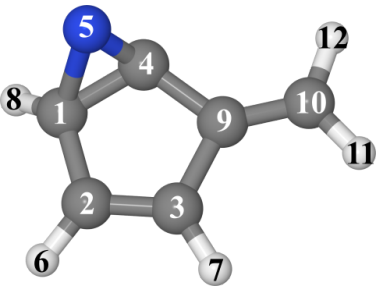
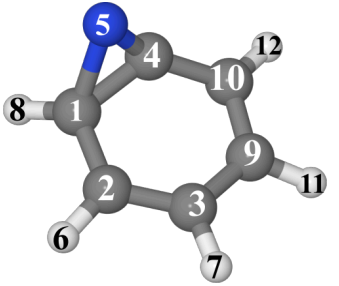
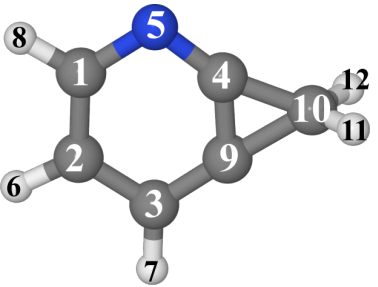
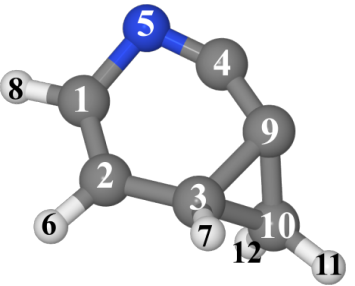
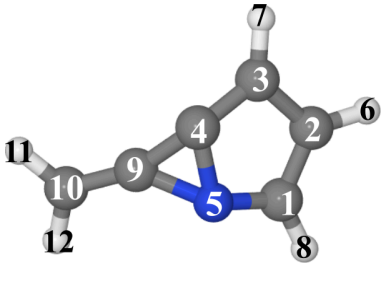
Also mentioned in chapter 2, LS cannot predict bond breaking interaction, and, although IRI offered some insights by presenting red regions between atoms. However, due to the qualitative nature of the isosurfaces, it is hard to evaluate which bond was truly weaker than the other, and thus, susceptible to breaking. Therefore, a numerical approach, which could precisely access the IRI ($sign(\lambda_2)\rho$) information between bonds is necessary to truly define weaker and stronger bonds.

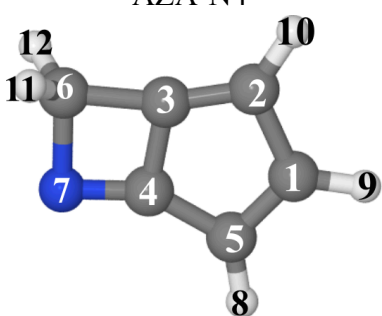
This information can be found in the output file `func1.cub` from Multiwfn. However, finding the values computed for the bond is not trivial given how a “cube” file is written. To do it, a Fortran program had to be written. The program is capable of reading the cube file, and given the pairs of atoms, it uses a simple linear approximation to interpolate the points of a line (the bond) between two points (the atoms) to the points of the $sign(\lambda_2)\rho$ grid, and then calculates an integral to define how repulsive this path is (see Appendix L for the code).

Below, Table J.7 brings the repulsiveness values in a line between two atoms m and n ($R_{m,n}$), for some steps where bond breaking information is regarded as important.

Table J.7. Repulsiveness in bonds calculated by IRI

Molecule	Bond	$R_{m,n}$
AZA-L	1-4	0.1287

	4-5	0.1664
	5-1	8.828×10^{-3}
AZA-P 	1-4	0.2459
	4-5	6.59×10^{-2}
	5-1	5.79×10^{-2}
AZA-O 	4-9	6.39×10^{-2}
	9-10	4.70×10^{-2}
	10-4	7.47×10^{-2}
AZA-W4 	3-9	1.10×10^{-2}
	9-10	7.60×10^{-2}
	10-3	1.40×10^{-2}
AZA-G 	4-5	5.76×10^{-2}
	5-9	3.97×10^{-2}
	9-4	0.116

	3-4	7.20×10^{-2}
	4-7	6.95×10^{-2}
	7-6	8.95×10^{-2}
	6-3	0.1053

For AZA-L this approximation finds C4-N5 as the most repulsive bond, thus possibly the weakest or most susceptible to breaking. This bond breaking would lead the molecule further from the target.

The weakest one for AZA-P is C1-C4, which leads the molecule back to a 7-atom ring. Here the breaking needed to reach the target would be N5-C1, which actually displayed the lowest repulsiveness.

Here, the results point that AZA-O is likely to go back to AZA-H as its weakest bond would be C4-C9. On the other hand, AZA-W4, that also comes from AZA-H has C9-C10 as the weakest bond, which would not lead it to AZA-W3 as IRC predicts.

AZA-G shows the possibility of breaking the bond C4-C9, which leads to a new molecule already predicted by IRC.

Finally, AZA-N4 weakest connection in its 4-atom ring is C3-C6, closely followed by C6-N7. The first bond breaking would lead to a quite unique molecule, the second one, however, simply pushes it back to AZA-N.

From these results it's clear that the linear approximation approach is rather rough. In particular for structures such as AZA-P which clearly display relevant repulsive interactions (at a 0.9 isosurface) that are not assessed by this approach, since it only considers a line (one dimension). A better approach would be to consider the line as the normal vector of a circle of radius around Bohr's radius (or a multiple of it) to build a cylinder (the bond), to then evaluate the values of $sign(\lambda_2)\rho$ it encapsulates.