THE NATURE AND APPLICATIONS OF SECONDARY INTERACTIONS IN MULTI-CENTER RADICAL π-DIMERS AND CONDUCTING POLYMERS

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By

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Multi-center π-radicals are a set of stable chemical species that are often used to construct new materials with promising magnetic and electric properties. In crystal structures, these radical species are often observed to dimerize by forming two-electron/multicenter (2e/mc) π-bonding, which is unusual since the bonding distances are much shorter than typical van der Waals contacts but significantly longer than conventional covalent bonds. Trimers and other aggregates are also observed. For conducting materials the quasi one dimensional chain-like π-stacked aggregates are especially important. One of the central questions of this dissertation is: what are the intermolecular forces that keep these aggregates together and how are these forces affecting the material properties?

With quantum mechanical calculations, we acquired new insight into the nature of the 2e/mc π-bonding formed by these radicals. By using a variety of theory levels, we found that proper descriptions of the static and dynamic electron correlations are necessary to account for the physical nature of the 2e/mc π-bonding. A significant charge shift bonding effect was found, which is attributed to the electron correlations between the nonbonding electron pairs and bonding electron pairs. By reducing the lone pair bond weakening effect (LPBWE) in phenalenyl dimers, we found that the 2e/mc π-bonding strength can be considerably enhanced, which makes
it promising to construct 2e/mc bonding with bonding strength approaching that of normal covalent bonds.

The importance of the 2e/mc bonding in \( \pi \)-dimers of multi-center radicals was also identified in pericyclic reactions. In 2,5,8-tri-tert-butyl-1,3-diazaphenalenyl \( \sigma \)-dimers, we computationally observed that the \( \sigma \)-bonds are fluxional and the \( \sigma \)-dimers can easily undergo a complete spectrum of sigmatropic rearrangement reactions via \( \pi \)-dimer intermediates, which gives rise to thermochromism as observed by experiments. In hydrogen transfer reactions of phenalene molecules, the multi-center phenalenyl radical dimers are important intermediates accounting for the stepwise ene-like reaction mechanism.

The physical properties of organic conducting polymers are usually correlated with \( \pi \)-conjugation. Our computational studies indicate that the intra-molecular noncovalent interactions also significantly affect the electronic structures of conducting polymers. Three types of noncovalent interactions were investigated in our studies, hydrogen bonding, noncovalent S···N interactions and \( \pi \)-\( \pi \) stacking. A series of low bandgap polymers were proposed based on intramolecular noncovalent interactions. In conjugated helicene polymers, we found electron communications arising from the transannular \( \pi \)-\( \pi \) interactions across the helical pitch. This property might be utilized for designing novel helicenes-based materials with unusual properties.
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CHAPTER 1
INTRODUCTION

The term “secondary interaction” is flexible and it usually refers to intermolecular interactions weaker than normal covalent bonds. The term typically includes hydrogen-bonding, electron donor-acceptor interactions, $\pi-\pi$ stacking, agostic bonding and so on. In this dissertation, we focus on the nature and applications of two types of secondary interactions. In the first category, the interactions occur between open shell molecular radicals. We ascribe them to intermolecular interactions instead of chemical bonds because those radicals are stable and they themselves are molecular entities like closed shell molecules. In the second category, we focus on the intramolecular interactions that are in nature analogous to the interactions between closed shell molecules.

Multicenter radicals are important chemical species that are often used to construct new materials with promising electrical and magnetic properties.\(^1\) Some of the multicenter radicals often seen in the literature are shown in Chart 1.1, which include phenalenyl radical, [TCNE]$^-$ (TCNE = teracyanoethylene) anion radical, [TCNQ] $^-$ (TCNQ = tetracyanoquinodimethane) anion radical, and [TTF] $^+$ (TTF = tetrathiafulvalene) cation radical. As shown in Chart 1.2, the singly occupied molecular orbitals (SOMOs) of those radical species are delocalized over multiple centers. Therefore, they are stable and can be experimentally observed in solids and in solutions.\(^2\)
Chart 1.1. The chemical structures of selected multicenter $\pi$-radicals.

![Chemical structures](image)

Chart 1.2. The SOMO orbitals of multicenter $\pi$-radicals.

![SOMO orbitals](image)

In crystal structures, these multicenter radicals often dimerize by forming $\pi$-dimers.\(^a\) The inter-dimer carbon-carbon (CC) distances are unusually shorter than typical van der Waals (vdW) CC contacts\(^{2b, 3}\) as shown in Figure 1.1. In this sense, there should be some chemical bonding that holds the two radical fragments together. On the other hand, the respective contact distances are too long to be considered as normal covalent bonds. A simple and intuitive description of such chemical bonding can be seen from the molecular orbital interaction diagram shown in Figure 1.2. The two SOMO orbitals overlap and split into a bonding highest occupied

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\(^a\) In this discussion we focus on dimers where these secondary interactions can be isolated. Other aggregations, such as trimers, and extended chains are well known. [See e.g. Extended Linear Chain Compounds Vol. 3 (Ed: Miller, J. S.), Plenum Press, New York, 1983.]
molecular orbital (HOMO) and an antibonding lowest unoccupied molecular orbital (LUMO). Since the two HOMO electrons are delocalized over multiple centers (mc), the respective bonding dimer interactions are usually called 2e/mc bonding. According to this model, the 2e/mc bonding is covalent. Moreover, ESR and NMR experiments also support the electron pairing in the \( \pi \)-dimers.\(^4\) In addition, there are specific favored relative packing geometries that indicate that the SOMO-SOMO bonding interactions are also essential.\(^5\) These favored orientations can be predicted by simply considering the maximum SOMO-SOMO overlap. This indicates that some aspects of this intermolecular \( \pi-\pi \) stacking interaction are analogous to covalent bonding. However, other evidence disfavors the covalent bonding argument for these dimers, such as the relative length of the bonding distances compared to ordinary covalent bond distance, the small interaction energies and electron depletion in the bonding region. That evidence points to the vDW nature of the stacking interactions in these radical \( \pi \)-dimers.\(^6\)

\[ D = 2.8 \, \text{Å} \]
\[ D = 3.3 \, \text{Å} \]

**Figure 1.1.** The structures of [TCNE]\(_2\)\(^{2-}\) (Ref. 3) and [phenalenyl]\(_2\) dimers showing the observed unusual contact distances (Ref. 2b).
Here, we seek understanding the nature of these 2e/mc bonding interactions (Chapter 3) as well as an approach to make the 2e/mc bonding more like a covalent bond (Chapter 2). In other words, is there a way to make a radical π-dimer with the bonding distances and binding energies approaching those of normal covalent bonds? The answers to these questions would help to clarify the nature of the 2e/mc bonding: are these covalent bonds or just vdW complexes? In previous studies of 2e/mc bonding, the covalent term has been broadly defined referring to the binding exclusive of vdW and electrostatic interactions. In our studies, we reexamined the nature of the covalency in 2e/mc bonding systems, and proposed some new insights into the nature of these unusual bonds.

Due to the delocalized character of the SOMOs, the multicenter radicals are often used to construct organic conductors, the properties of which are closely related to the π-π stacking of those radicals in the solid state. The investigation of the bonding nature for those radical π-dimers help to understand the behavior of π-π stacking of those radicals in crystals, and hence would be beneficial to find ways to control the physical properties of those π-radical based
materials. Better understanding of the factors affecting 2e/mc bonding will also provide opportunities to design new radical motifs used as building blocks for new materials.

Another focus of multicenter $\pi$-radicals is their involvement in pericyclic reactions. Due to the stability and formation of 2e/mc bonding of those radicals, we found that they are closely related to the stepwise mechanism of the chemical reactions involved by phenalenyl derivatives. The mechanistic studies of those reactions can help to explain many experimental observations such as thermochromism in the crystals of 2,5,8-tri-tert-butyl-1,3-diazaphenalenyl (Chapter 4) and H-transfer (Chapter 5).

In the project about organic semiconducting polymers, we addressed the intramolecular noncovalent interactions in conducting polymers (Chapter 6-8). It is known that the physical properties such as the band gaps and charge mobility are highly correlated with the $\pi$-conjugation of the conducting polymers. In $\pi$-conjugated polymers, the molecular orbital levels of the monomers disperse into broad $\pi$-bands, thereby narrowing the energy gap between the highest occupied (HO) and the lowest unoccupied (LU) energy level. The high degree of $\pi$-electron conjugation and good frontier orbital overlap between neighboring unit cells generally favor a larger $\pi$-bandwidth and a smaller band gap.

However, we found that intramolecular noncovalent interactions can also significantly affect the electronic structures of conducting polymers. Three types of noncovalent interactions are investigated in this project: hydrogen bonding, S…N interactions and $\pi-\pi$ stacking. Those three type interactions widely exist in crystal structures, but their involvement in conducting polymers is rarely investigated. Compared to modification through chemical bonds, the noncovalent
approach is more flexible to control of the properties of the extended materials. Based on those noncovalent interactions, a series of low gap polymers were proposed.

The dissertation is organized as follows. In Chapter 2 and 3, we validated the computational methods for the 2e/mc bonding systems by comparing calculations with experimental bonding distances and interaction energies. The factors affecting the bonding strength are discussed and a set of new radical $\pi$-dimers are proposed with highest recorded bonding strength. The novel charge shift bonding concept\textsuperscript{7}, as introduced by Shaik et al., is applied to the radical $\pi$-dimers with the purpose of gaining new insights into the nature of 2e/mc bonding. In Chapter 4 and 5, we show the application of 2e/mc bonding to pericyclic reactions with an emphasis on the mechanism of the stepwise sigmatropic rearrangement and hydrogen transfer reactions. In Chapter 6, 7 and 8, we discuss how the electronic structures of conducting polymers are influenced by intramolecular noncovalent interactions focusing on $\pi$-$\pi$ stacking in helicenes (Chapter 6), hydrogen bonding in pyrazine polymers (Chapter 7), and S…N interactions in polyenazine (Chapter 8). Chapter 9 is somewhat independent, but it is related to Chapter 8. In this chapter, we propose a design of molecular actuators based on secondary S…N interactions.

References


CHAPTER 2

IS THERE A LOWER LIMIT TO THE CC BONDING DISTANCES IN NEUTRAL RADICAL π-DIMERS?

THE CASE OF PHENALENYL DERIVATIVES*

Chemical bonding is one of the most fundamental concepts in chemistry. In a normal two electron two center (2e/2c) covalent C–C bond, the bond formation can be qualitatively described by in-phase overlap of the two hybrid atomic radical orbitals in a molecular orbital (MO) diagram, or in valence bond (VB) parlance it can be regarded as the resonance interactions between the two covalent spin pairing patterns C(sp$^3$)$^\uparrow$C(sp$^3$)$^\downarrow$ and C(sp$^3$)$^\downarrow$C(sp$^3$)$^\uparrow$.$^1$ At the other extreme, for long carbon-carbon (C(sp$^2$)…C(sp$^2$)) contacts, as in graphite, the weak bonding is attributed to van der Waals (vdW) interactions. There is a wide ‘forbidden’ zone between covalent bond and the shortest vdW contact. For CC contacts this forbidden zone extends from approximately 1.75 Å (as in stretched C–C bonds$^2$) to 2.806 Å (as in [TCNE]$^2^-$).$^3$ Can molecules be imagined, and perhaps be made that show contacts in this hitherto forbidden zone? What interesting properties would such molecules exhibit?

Phenalenyl (PHYL) is a neutral π-radical that has been used recently to construct organic conductors.$^4$ Neutral and charged π-radicals often form stacked π-dimers with 2 electron/multicenter (2e/mc) bonding while in the highly conducting phases the electrons tend to delocalize over the material. The SOMOs (singly occupied molecular orbitals) of these radicals are delocalized over multiple sites as shown in Scheme 2.1.$^4$ In the MO description, the π-dimer

---

is stabilized by forming 2e/12c bonding through in phase SOMO-SOMO overlap as shown in Scheme 2.1, which is supported by NMR studies.\textsuperscript{5} This dimer formation is accompanied by special 2e/12c bonding distances (3.10-3.30 Å) that are much longer than normal C–C bonds and significantly shorter than typical vdW contacts (3.45 Å), and interaction energies are much weaker than for normal covalent bonds.\textsuperscript{6} For charged π-dimers such as [TCNQ]\textsubscript{2}\textsuperscript{2−} and [TTF]\textsubscript{2}\textsuperscript{2+}, the dominant interactions holding the dimers together are electrostatic forces from counterions and the dispersion forces between the dimers.\textsuperscript{7} For the neutral [PHYL]\textsubscript{2} π-dimers the dominant bonding contribution is from the dispersion force between the two fragments.\textsuperscript{6,8} These characteristics weaken the argument to regard the 2e/mc bonding as covalent. It has been suggested that these π-dimers have characteristics that are closer to van der Waals complexes than to covalent bonding.\textsuperscript{8} The shortest 2e/mc bonding of 2.806 Å occurs in a [TCNE]\textsubscript{2}\textsuperscript{2−} π-dimer,\textsuperscript{3} but the electrostatic cation-anion interactions dominate its binding energy.\textsuperscript{9} Can a neutral covalent π-dimer be found that pushes the 2e/mc bonding distances towards the shortest possible values and dimer interaction energies towards the largest possible values by means of chemical modifications of the radical π-dimers without becoming a σ-bond?

**Scheme 2.1.** The singly occupied molecular orbital (SOMO) of phenalenyl radical (a) and the highest occupied molecular orbitals of phenalenyl π-dimer (b).
In this study, we introduced a series of $\beta$-substituted neutral PHYL $\pi$-dimers with the purpose to answer these questions and to better understand the factors affecting the interactions that underlie these unusually short contacts. Both our density functional theory (DFT) and ab initio calculations show that these substituted $\pi$-dimers have considerably stronger bonding energies and significantly shorter bond distances than the parent PHYL $\pi$-dimer and shorter than any previously reported $\pi$-dimer.\textsuperscript{10} We also show that the covalent contributions to the 2e/12c bonding can be substantially stronger than that of the parent dimer.

Since the SOMO density is localized on the $\alpha$-positions, the $\alpha$-substitutions offer a natural strategy to modify the properties of PHYL $\pi$-dimers, and actually most of the PHYL derivatives in the literature are $\alpha$-substituted.\textsuperscript{[11]} However, in this study, we found that the $\beta$-substitutions are more effective to strengthen the 2e/12c bonding. The structures of the target systems are listed in Scheme 2.2: 2-6 are $\beta$-substituted, and 7-8 are $\alpha$-substituted. The NO$_2$ and BR$_3$ groups were not included for $\alpha$-substitution for steric reasons. One characteristic of the $\beta$-set is that the SOMO patterns are unchanged due to the nodal pattern (Scheme 2.1), while for the $\alpha$-set, the SOMOs are perturbed by the substituents. We denoted the dimers both with the labels and substituents, for example, 2$_2$(CN); the subscript 2 representing a dimer. All dimers are staggered in the calculations.

The M05-2X\textsuperscript{12,13} density functional method was used for geometry optimization. Interaction energies\textsuperscript{14} were calculated by the M05-2X DFT\textsuperscript{15} and MRPT2/CASSCF(2,2)\textsuperscript{16,17,18} methods. Both methods include dynamic electron correlations, and perform well for 2e/12c bonding in $\pi$-
dimers.\textsuperscript{7, 19} In particular, the M05-2X calculations for PHYL $\pi$-dimers have shown excellent agreement with experiments in terms of geometries and interaction energies (See Chapter 4).\textsuperscript{20}

The calculated bond distances and the binding energies are tabulated in Table 2.1 for the $\beta$-substituted dimers in comparison with the parent PHYL dimer \textit{1$_2$(H)}. We noticed that upon $\beta$-substitutions, the interaction energies are significantly enhanced, and bond distances are remarkably reduced compared to \textit{1$_2$(H)}. Although there are differences in binding energies by using the two methods, the trend is same.

\textbf{Scheme 2.2.} The structures of the beta-modified PHYL derivatives used to construct $\pi$-dimers in the study.

Upon substitutions, the strongest bonding occurs in the dimer \textit{5$_2$(NBH$_3$)}. The interaction energy is as high as 31.57 kcal mol$^{-1}$ by the M05-2X method, and the calculated bond distance of 2.744 Å is the shortest in the PHYL dimer family. One noticeable observation is that the differences between $R_1$ (the intradimer C$_\alpha$–C$_\alpha$ distance) and $R_2$ (the central carbon distance)
increase with increasing bond strength, which is indicative of stronger attractive forces between α-carbon pairs than between central carbon pairs. This is strong evidence for the presence of covalent bonding due to SOMO electron pairing.

Table 2.1. The interaction energies ($E_{int}$ in kcal mol$^{-1}$) and contact distances ($R^a$ in Å) of the β-substituted PHYL π-dimers.

<table>
<thead>
<tr>
<th></th>
<th>UM05-2X</th>
<th>MRPT2[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_1$</td>
<td>$R_2$</td>
</tr>
<tr>
<td>$1_2$(H)</td>
<td>3.124</td>
<td>3.161</td>
</tr>
<tr>
<td>$2_2$(CN)</td>
<td>2.967</td>
<td>3.091</td>
</tr>
<tr>
<td>$3_2$(NO$_2$)</td>
<td>2.896</td>
<td>3.048</td>
</tr>
<tr>
<td>$4_2$(N)</td>
<td>2.821</td>
<td>2.990</td>
</tr>
<tr>
<td>$5_2$(NBH$_3$)</td>
<td>2.744</td>
<td>3.029</td>
</tr>
<tr>
<td>$6_2$(NBMe$_3$)</td>
<td>2.825</td>
<td>2.937</td>
</tr>
</tbody>
</table>

$^a R_1$ and $R_2$ are the intradimer distances between the α-carbons and central carbons, respectively.

$^b$ The single point calculations at the UM05-2X optimized geometries.

Table 2.2. The M05-2X calculated interaction energies ($E_{int}$ in kcal mol$^{-1}$) and bond distances ($R^a$ in Å) of the α-substituted PHYL π-dimers.

<table>
<thead>
<tr>
<th></th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$E_{int}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1_2$(H)</td>
<td>3.124</td>
<td>3.161</td>
<td>-8.87</td>
</tr>
<tr>
<td>$7_2$(CN)</td>
<td>3.209</td>
<td>3.256</td>
<td>-9.69</td>
</tr>
<tr>
<td>$8_2$(N)</td>
<td>3.196</td>
<td>3.270</td>
<td>-6.09</td>
</tr>
</tbody>
</table>

$^a R_1$ and $R_2$ are defined in Table 2.1.
The interaction energies and distances for the α-series 7-8, are summarized in Table 2. Compared to the parent PHYL dimer 12(H), the bonding strengths and distances do not change very much upon α-substitutions. This is because for dimer 72(CN), the SOMO density delocalizes to the attached substitutes leading to reduced SOMO-SOMO overlap as shown in Figure 2.1. For dimer 82(N), despite the smaller atomic radius of nitrogen, the closest contacts are even longer than that of 12(H), which is due to the reduced SOMO-SOMO overlap.

![Figure 2.1. The SOMOs of phenalenyl (left) and CN-substituted phenalenyl (right)](image)

In order to assess the role of multipole-multipole interactions and dispersion forces on the bond distance shortening and bond strength reinforcement upon β-substitutions, the dimers composed of the structures 9-14 in Scheme 2.3 were adopted.8 Note that these structures are the closed shell counterparts of the structures 1-6. The multipole and dispersion forces are expected to be similar in magnitude to those in 12-62, and hence can be used as indicators of those forces in the β-substituted neutral radical PHYL dimers. The respective optimized geometrical parameters and interaction energies are summarized in Table 2.3. Compared to dimer 92, the
interaction energies upon β-substitutions do not change much for the closed shell dimers. Accordingly, the possibility is ruled out that the bonding fortification of those derivative PHYL dimers 2-6 are due to the changes of multipole and dispersion forces upon β-substitutions.

**Scheme 2.3.** The structures of the 9b-azaphenalene (9) and the corresponding β-substituted derivatives.

![Scheme 2.3](image)

**Table 2.3.** The M05-2X calculated interaction energies ($E_{int}$ in kcal mol$^{-1}$) and bond distances between α-sites ($R$ in Å) of the closed shell dimers 9-14.

<table>
<thead>
<tr>
<th></th>
<th>$R$</th>
<th>$E_{int}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9$_2$(H)</td>
<td>3.670</td>
<td>-3.73</td>
</tr>
<tr>
<td>10$_2$(CN)</td>
<td>3.608</td>
<td>-5.78</td>
</tr>
<tr>
<td>11$_2$(NO$_2$)</td>
<td>3.578</td>
<td>-2.87</td>
</tr>
<tr>
<td>12$_2$(N)</td>
<td>3.418</td>
<td>-5.88</td>
</tr>
<tr>
<td>13$_2$(NBH)</td>
<td>3.261</td>
<td>-14.63</td>
</tr>
<tr>
<td>14$_2$(NBMe)</td>
<td>4.128</td>
<td>-12.35</td>
</tr>
</tbody>
</table>
In a previous study, the covalent bonding contribution was shown to be small in PHYL dimers\textsuperscript{8}. Given the wide range of interaction energies obtained in this study we are intrigued by the role of covalent bonding in the newly introduced neutral radical $\pi$-dimers. Any analysis that refers to the decomposition of the interaction energy contains arbitrary elements, yet such an analysis is helpful for obtaining patterns of understanding and predicting trends. If we treat the $\pi$-dimer as a two electron model analogous to the prototypical H–H bond, within the Heitler-London approximation the ground state energy $E_{\text{GS}}$ and the triplet state energy $E_T$ are expressed as:

\[
E_{\text{GS}} = \frac{\left(\epsilon_a + \epsilon_b + Q + K\right)}{(1+S^2)} + \frac{1}{R}
\] \hspace{1cm} (2.1)

\[
K = (2\beta S + K_{ab})
\] \hspace{1cm} (2.2)

\[
E_T = \frac{\left(\epsilon_a + \epsilon_b + Q - K\right)}{(1-S^2)} + \frac{1}{R}
\] \hspace{1cm} (2.3)

where $\epsilon_a$ and $\epsilon_b$ are the SOMO energies of two separated radical fragments, $Q$, $K_{ab}$, $\beta$, and $S$ are the Coulomb integral, exchange integral, resonance integral and bonding or orbital overlap, respectively. The “exchange” term $K$ in eq. (2.2) represents the covalent bonding arising from the coupling of two radical electrons\textsuperscript{22}. We used this term to characterize the covalent component of the interaction energy. The exchange term $K$ can be estimated when $S$ is small as:

\[
K = \frac{1}{2}(E_{\text{GS}} - E_T)
\] \hspace{1cm} (2.4)

wherein $E_{\text{GS}}$ and $E_T$ were calculated with CASSCF(2,2) based on the same geometries. The VB (HL) wavefunctions corresponding to the singlet and triplet of the two electron model can be described in the equations 2.5 and 2.6, respectively. A similar approach has been used to decompose the interaction energy of the 2,5,8-tri-tert-butyl-phenalenyl $\pi$-dimer.\textsuperscript{8}
The covalent component of the interaction energy is listed in Table 2.4 for the neutral radical \( \pi \)-dimers under discussion. \(|K| \) increases with increasing total interaction energy. For \( 5_2(\text{NBH}_3) \), \(|K| \) is almost double of that of the parent PHYL dimer \( 1_2(\text{H}) \) providing direct evidence that covalent bonding plays a key role in holding the dimer together, although the total interaction is weakened by some repulsive forces as discussed below. The greatly enhanced covalent bonding in the new \( \pi \)-dimers indicates that carbon based 2e/12c covalent bonding might be constructed with bond strength further approaching normal C–C bonds.

Table 2.4. The covalent interaction energy components (\( K \) in kcal mol\(^{-1}\)) for neutral radical dimers.

<table>
<thead>
<tr>
<th></th>
<th>( 1_2(\text{H}) )</th>
<th>( 2_2(\text{CN}) )</th>
<th>( 3_2(\text{NO}_2) )</th>
<th>( 4_2(\text{N}) )</th>
<th>( 5_2(\text{NBH}) )</th>
<th>( 6_2(\text{NBMe}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-10.21</td>
<td>-14.84</td>
<td>-17.14</td>
<td>-19.08</td>
<td>-21.94</td>
<td>-19.34</td>
</tr>
</tbody>
</table>

Next we explored some factors affecting the strength of the interaction. For the series of PHYL derivatives 1-6, the substituents are only situated at the \( \beta \)-positions, which are at the nodes of the SOMO. Accordingly, the node patterns of the SOMO are not perturbed upon
substitutions, and the SOMO populations at the bonding sites (i.e. the α-site) are same for all these dimers (as shown in Figure 2.1). This excludes the effect of the SOMO-SOMO overlap populations localized at the bonding sites. Note that all substituents discussed here are electron withdrawing compared to hydrogen. The inductive effect of the CN and NO$_2$ groups withdraw electron density through the C$_\beta$–C$_\alpha$ σ bonds. In addition, the resonance effect withdraws π-electrons from the conjugated PHLY plane. Both of these effects reduce the electron density at the α-carbons. The calculated NPA (natural population analysis) charges are listed in Table 2.5.

**Table 2.5.** The NPA atomic charges (e) on the α-carbons of the PHYL derivatives. $^a$

<table>
<thead>
<tr>
<th></th>
<th>NPA</th>
<th>π$^b$</th>
<th>σ$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(H)</td>
<td>-0.20 (0.00)$^d$</td>
<td>+0.01 (0.00)</td>
<td>-0.21 (0.00)</td>
</tr>
<tr>
<td>2(CN)</td>
<td>-0.14 (0.06)</td>
<td>+0.05 (0.04)</td>
<td>-0.19 (0.02)</td>
</tr>
<tr>
<td>3(NO$_2$)</td>
<td>-0.17 (0.03)</td>
<td>+0.09 (0.08)</td>
<td>-0.26 (-0.05)</td>
</tr>
<tr>
<td>4(N)</td>
<td>+0.07 (0.27)</td>
<td>+0.09 (0.08)</td>
<td>-0.02 (0.19)</td>
</tr>
<tr>
<td>5(NBH)</td>
<td>+0.13 (0.33)</td>
<td>+0.13 (0.12)</td>
<td>0.00 (0.21)</td>
</tr>
<tr>
<td>6(NBMe)</td>
<td>+0.13 (0.33)</td>
<td>+0.13 (0.12)</td>
<td>0.00 (0.21)</td>
</tr>
</tbody>
</table>

$^a$ UM05-2X/6-31G(d) method.

$^b$ π-electron contribution.

$^c$ σ-electron contribution.

$^d$ The numbers in parenthesis are charges relative to 1(H).
Compared to the parent PHYL, there is a significant reduction of the total electron density at the $\alpha$-carbons in 2, 3, 4, 5 and 6. For 4(N), the reduction of electron density is more significant than that for 2(CN) and 3(NO$_2$). For the hypothetical dimers 5$_2$(NBH$_3$) and 6$_2$(NBMe$_3$), a dative bond forms between the sp$^2$ lone pair of the $\beta$-nitrogen and the empty orbitals of the boron, which results in an even stronger reductive effect for 5 and 6 compared to 4(N) as shown by the NPA charges in Table 2.5.

From Table 2.1 and Table 2.5, it is noted that the reduction of electron density at the $\alpha$-carbons correlates with stronger 2e/12c bonds. This can be qualitatively explained by the lone pair bond weakening effect (LPBWE), which exists in diatomic covalent bonds composed of electron rich elements like F–F and HO–OH. For the parent PHYL radicals, the SOMO can be viewed as the radical orbital of F or HO, and the electrons from the remnant $\pi$-electrons and the electrons from the $\sigma$-bond behave as lone pairs. Accordingly, the LPBWE effect is expected to be strong in the parent PHYL dimers. It accounts for the noncovalent Coulomb repulsions and Pauli repulsions, which weakens the total interaction energies of the dimers. With the introduction of electron withdrawing groups, the electron density on the $\alpha$-carbons decreases. Consequently, the LPBWE effect between the SOMO electron and the “lone pairs” at the $\alpha$-carbons is reduced, which gives rise to stronger 2e/12c bonds. This indicates that the 2e/mc bonds in the $\pi$-dimers might come closer to normal C-C bond upon proper substitutions. However, further quantitative investigations are needed to understand the origin of the strong covalent energetic components in the substituted PHYL dimers, specifically the charge density fluctuations represented by the "pure" covalent and ionic mixing according to VB description.
The ratio of the SOMO-SOMO splitting ($2|t|$) to the Hubbard on-site Coulomb repulsion ($U$) is an important parameter determining electron localization and thereby many properties of organic conductors. For the presented series of neutral $\pi$-radical dimers, the approximate $2|t|/U$ values are shown in Table 2.6. $U$ was estimated by the equation\(^{25,26}\):

$$U = S_0 + S_2 - 2T$$

which is derived based on simplified Hubbard model for two electron dimer model.

$$S_0 = \frac{U}{2} (1 + A) + C$$ \hspace{1cm} (2.8)

$$S_2 = \frac{U}{2} (1 - A) + C$$ \hspace{1cm} (2.9)

$$T = 0 + C$$ \hspace{1cm} (2.10)

$$A = \sqrt{1 + \left(\frac{4t}{U}\right)^2}$$ \hspace{1cm} (2.11)

where $S_0$, $S_2$ and $T$ are the energies of the ground state, the second excited singlet state (corresponding to the double excitation to the LUMO), and the first excited triplet state, respectively. Note, that $U$ is relatively constant because the SOMO pattern remains essentially constant upon $\beta$-substitutions. On the other hand, the SOMO-SOMO splittings considerably depend on the intermolecular packing in the dimer. Therefore, the substituted PHYL dimers are predicted to have much larger $2|t|/U$ than the parent dimer $1_2(H)$. By being able to raise this value by about a factor of two and above the critical value of 1.0\(^4\), the properties of the solids made from these radicals might display profoundly different and possibly novel properties.
Table 2.6. The Coulomb repulsions ($U$), the SOMO-SOMO splittings ($|t|$) and the ratios of $2|t|/U$.

|       | $U$/eV | $|t|$/eV$^{26}$ | $2|t|/U$ |
|-------|--------|----------------|---------|
| $1_2$(H) | 1.71   | 0.58           | 0.68    |
| $2_2$(CN) | 1.46   | 0.73           | 1.00    |
| $3_2$(NO$_2$) | 1.42  | 0.80           | 1.13    |
| $4_2$(N)  | 1.53   | 0.88           | 1.15    |
| $5_2$(NBH) | 1.28   | 0.86           | 1.34    |
| $6_2$(NBMe) | -     | 0.87           | -       |

The above discussion shows that the electron withdrawing groups make the 2e/mc bonding stronger. One may ask if there is a reverse trend that electron donating groups such as methyl and amino groups make the bonding weaker. Methyl and amino groups, which are generally thought of as electron-donating groups, and hence weaker dimer bonding was expected for $\beta$-substitutions with these substituents. However, as shown in Scheme 2.4, our calculations indicate that methyl and amino groups overall pull electrons from the PHYL molecule. Correspondingly, these groups tend to affect the multicenter $\pi$-bonding similarly to other more obvious electron withdrawing groups, such as –CN group in connection with the data given in Table 2.1. This is not surprising taking into account the relatively higher electron negativity of C and N, relative to H. The data presented in Table 2.7 reflect the result of these substitutions. Although, methyl
groups and amino groups might donate electrons to the PHYL π-ring through hyperconjugation and π-conjugation, the relative high electronegativity make them overall electron-withdrawing in comparison with H.

**Scheme 2.4.** The structures of β-tri-methyl and β-tri-amino substituted PHYL. The NPA atomic charges are shown for α and β carbons.

![Scheme 2.4](image)

**Table 2.7.** The calculated bonding distances ($R_1$ in Å), bonding energies ($E_{int}$ in kcal/mol), and the Coulomb repulsion parameters ($U$ in eV)

<table>
<thead>
<tr>
<th></th>
<th>$R_1$</th>
<th>$E_{int}^{a,b}$</th>
<th>$E_{int}^{a,c}$</th>
<th>$U$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>2.959</td>
<td>-12.18</td>
<td>-13.33</td>
<td>1.49</td>
</tr>
<tr>
<td>16</td>
<td>2.890</td>
<td>-17.26</td>
<td>-19.68</td>
<td>1.44</td>
</tr>
</tbody>
</table>

* $R_1$ is the Cα-Cα distance. Geometry optimized by UM052X/6-31+G(d,p);
* $E_{int}$ calculated by UM052X/6-31+G(d,p);
* $E_{int}$ calculated by MRMP2/6-31G(d).
Acknowledgement.

We thank the U. S. National Science Foundation for its support of this research.

References


(a) The spin-unrestricted broken symmetry (BS) scheme was used for the DFT calculations. The BS solutions different from the spin-restricted solutions were obtained only for the parent 12(H) dimer and the dimer 22(CN). (b) Vibrational frequency calculations (at UM05-2X/6-31G(d,p)// UM05-2X/6-31G(d,p) level) were performed for each stationary point to identify it as a minimum.

631+G(d,p) and 6-31G(d) basis set were used for DFT and MRMP2 method, respectively.

(a) All DFT calculations are performed with Gaussian 03. (b) M. J. Frisch, et al. Revision E. Gaussian, Inc.: Pittsburgh, PA, 2007.

The active space included the highest occupied orbital (HOMO) and the lowest unoccupied orbital (LUMO).


(a) The $E_{\text{int}}$ is defined as: $E = E_{\text{opt}} - E_{8.00}$, where $E_{\text{opt}}$ and $E_{8.00}$ is the total energy at the optimized geometry and at the separation of 8.00 Å, respectively. (b) $R$ is the interphenalenyl $C_{\alpha}-C_{\alpha}$ distance; basis set superposition error was corrected by the counterpoise scheme.


24 This might be associated with the charge-shift bond concept proposed by Shaik and Hiberty et al., see ref. 23c.


26 $S_0$, $S_2$ and $T$ were calculated by using state averaged MCQDPT/ CASSCF(2,2). $2|\sigma|$ is the HOMO-LUMO gap of the dimer calculated at the PW91/6-31G(d,p) level. $U$ is based on the dimer calculation and is therefore the “effective” $U=U_0-U_1$, where $U_0$ is the on site, and $U_1$ is the first neighbor Coulomb repulsion.
3.1. Introduction

Multicentered bonding formed between \(\pi\)-radicals has been observed in the X-ray crystal structures of many \(\pi\)-radicals. In those radical species, the singly occupied molecular orbitals (SOMO) are delocalized over multiple centers due to \(\pi\)-conjugation, and hence those chemical species can be relatively stable. In radical \(\pi\)-dimers, as depicted by Scheme 3.1, the two fragmental SOMOs overlap and split into a bonding highest occupied molecular orbital (HOMO) occupied by two electrons and an unoccupied lowest molecular orbital (LUMO).

**Scheme 3.1.** Molecular orbital interaction diagram showing the formation of 2e/mc bonding in radical \(\pi\)-dimers. SOMO stands for singly occupied molecular orbitals of the constituent radicals.

It is suggested that radical fragments are held at bonding distances shorter than typical van der Waals (vdW) contacts due to the formation of a 2-electron/multicenter (2e/mc) bonding HOMO orbitals, as shown in Figure 3.1. In this sense, the 2e/mc bondings in the radical \(\pi\)-dimers are
similar to covalent bonds. In addition, the NMR experiments also indicate that the two SOMO electrons are paired in the \( \pi \)-dimers.\(^3\) This evidence supports the covalent nature for those radical \( \pi \)-dimers.

![HOMO orbitals of [TCNE]_{2}^{2-} and [phenalenyl]_{2} dimers obtained by Hartree-Fock/6-31G* calculations at bonding distances of 2.89 Å and 3.30 Å, respectively.](image)

**Figure 3.1.** The HOMO orbitals of [TCNE]_{2}^{2-} and [phenalenyl]_{2} dimers obtained by Hartree-Fock/6-31G* calculations at bonding distances of 2.89 Å and 3.30 Å, respectively.

On the other hand, there exist many features disfavoring the arguments for covalent bonding. First, the carbon-carbon (CC) bonding distances in the dimers seem too long to be covalent when compared with normal covalent CC bonds (~1.54 Å).\(^4\) Secondly, the 2e/mc bonds are much weaker compared to conventional CC bonds. For instance, the dissociation energies of tri-\textit{tert}-butyl-phenalenyl \( \pi \)-dimers and [TCNE]_{2}^{2-} \( \pi \)-dimers are only about 7.5-9.5 kcal/mol\(^5,6\) and 8.8 kcal/mol\(^7\), respectively. Thus, the bond dissociation energies fall into a range of typical vdW interactions associated with \( \pi-\pi \) stacking. From this perspective, these radical \( \pi \)-dimers seem to be vdW complexes.\(^8\)

In this study, we aim to gain insight into the nature of the 2e/mc bonding by using quantum mechanical calculations. By recognizing analogies between F–F (difluorine, F\(_2\)) bonds and
2e/mc bonding in radical π-dimers, we demonstrate that the bonding concept for F–F is applicable to the radical π-dimer systems.

F–F and 2e/mc bonding systems are analogous with respect to the following aspects. First, both type of bonding are weak compared to normal covalent bonds. The bonding energies of F–F is only about 38 kcal/mol, and that of the strongest 2e/mc bonding is about 30 kcal/mol as shown by a hypothetical phenalenyl dimer in Chapter 2. Secondly, they both comprise electron rich fragments. In F–F, there are three lone pairs on each bonding center. In 2e/mc systems, for example [TCNE]22– and [PHYL]22, there are one or six “lone pairs” on each fragment, if the nonbonding π-orbitals are viewed as lone pairs. Thirdly, at the Hartree-Fock level, they both show repulsive interactions, which implies that the bonding in these two systems should be much different from normal covalent bonds. Another remarkable feature is that electron density analysis shows electron depletion in the bonding region as reflected by the positive or close to zero Laplacian at the bond critical points as shown in Figure 3.2. This is in contrast to the negative Laplacian of the normal covalent bonds like hydrogen molecule, H–H.

![Figure 3.2.](image)

**Figure 3.2.** The structures of TCNE₂²⁻, F–F and H–H and the Laplacians of the total electron density at the corresponding bond critical points.
Given the similarities between the two systems, the bonding concept for F–F might be applicable to 2e/mc π-dimers. For this reason, we take a brief review of the nature of chemical bonds for F–F.\textsuperscript{10} In a recent valence bond (VB) study, Shaik et al.\textsuperscript{10} showed by referring to the data shown in Figure 3.3, that the bonding attraction in H–H molecules mostly arises from the covalent structure. However, for F–F, the molecule is repulsive if only the covalent structure is included in the VB calculations. By using the breathing orbital VB (BOVB) method, they found that the dynamic mixing of the covalent structures and ionic structures contributes to the bonding for F–F as diagrammatically outlined by the orbitals in Scheme 3.2. In this approach, the three VB structures use different set of orbitals, and the orbitals are allowed to relax to reflect the local field for the corresponding VB structures.\textsuperscript{11} Note that the corresponding lone pair orbitals become more diffuse when the bonding electron pair is localized on the same center. Thus, the bonding electron pairs are dynamically correlated with the lone pairs. To reflect such character, they call it charge shift (CS) bonding.

**Scheme 3.2.** Orbital diagram for breathing orbital VB (BOVB) description of chemical bonding in F–F. The lobes represent the electron lone pairs and the bonding pair (sp\textsuperscript{3} hybridized orbitals are used.) The enlarged lobes on F and the reduced size lobes on F\textsuperscript{+} indicate the variable (breathing) orbitals on the formally charged atoms.

\end{document}
Figure 3.3. The bonding dissociation curve for H-H and F-F calculated by using purely covalent structures (dash line) and the mixed covalent and ionic structures (solid line) (Ref.10b).

Herein, we demonstrate that there is a significant charge shift contribution to the chemical bonding in [TCNE]$_2^{2-}$ dimers. Due to the similarities of the electronic structures, the bonding concept manifested by [TCNE]$_2^{2-}$ might be insightful to understand the nature of other radical π-dimers. In the previous studies in Chapter 2, we have proposed that there might be some connections between the lone pair bond weakening effect (LPBWE) and the charge shift effect in those phenalenyl π-dimers with short bonding distances. However, due to the large number of nonbonding π-electrons around the bonding active SOMO electrons, it is computationally challenging to demonstrate that effect in phenalenyl dimer systems. In this chapter, the investigation for [TCNE]$_2^{2-}$ dimer, a smallest 2e/mc system, might provide an opportunity to demonstrate the charge shift bonding concept of this class of radical π-dimers.
3.2 Methodology

Although the BOVB calculations clearly show the charge shift effect in F–F, this method is limited to systems with only a small number of electrons due to nonorthogonality of the orbitals. To overcome this difficulty for larger molecular systems, as well as to evaluate the charge shift effect with a complementary methodology, the generalized valence bond (GVB) based restricted configuration-interactions (GVB-RCI) was proposed as an alternative to manifest the charge shift effect for F–F.$^{12}$ Actually, the similar calculations have been carried out to calculate electron affinity$^{13}$ of electron rich systems like OH•, and to calculate the charge transfer state of ethylene molecules$^{14}$. In those previous studies, the authors addressed the importance of dynamic electron correlations between the bonding electron pairs and electron pairs corresponding to the core part of the wavefunctions.

In this section, we qualitatively inspect the origin of why Hartree-Fock and complete active space self-consistent field (CASSCF(2,2)) fail to describe the bonding behavior for 2e/mc bonding systems, and demonstrate how the GVB-RCI methodology can recover a significant portion of the dynamic electron correlation corresponding to the charge shift effect in [TCNE]$^{2-}$ dimers. The [TCNE]$^{2-}$ dimer are used as a model system because there are only a small number of $\pi$-electrons in this system. Considering only the two active $\pi$-electrons (the two radical electrons on the SOMOs as shown in Scheme 3.3.) related to the 2e/mc bonding, the wavefunction corresponding to the covalent pairing can be written$^{12}$ as the following within the VB scheme,

$$\Psi_c = (|\chi_A\chi_B > - |\chi_A\chi_B >)/\sqrt{2}$$

(3.1)
in which there is one electrons on each center A and B. A and B denote the two radical $[\text{TCNE}]^-$ fragments in the dimers. $\chi_A$ and $\chi_B$ are the SOMO orbitals (Scheme 3.3) localized on fragments A and B, respectively. This wavefunction represents a pure covalent term or a diradical singlet state.

**Scheme 3.3.** The SOMO orbital of $\text{TCNE}^-$

The pure ionic terms can be described by the following two equations,

$$\Psi_I = (|\chi_A \chi_A^- > - |\chi_B \chi_B^- >)/\sqrt{2}$$  \hspace{1cm} (3.2)

$$\Psi_{I'} = (|\chi_A \chi_A^- > + |\chi_B \chi_B^- >)/\sqrt{2}$$  \hspace{1cm} (3.3)

In both of the terms, the two active electrons are simultaneously on the same centers. $\Psi_I$, which has a $u$ symmetry, corresponds to the lowest ionic state. The ground state ($A_g$) of the dimer can be obtained by mixing the covalent term and ionic term with $A_g$ symmetry.

$$\Psi = c_1 \Psi_c + c_2 \Psi_I$$  \hspace{1cm} (3.4)

Within the molecular orbital (MO) scheme, the bonding and antibonding orbitals in the $[\text{TCNE}]_2^{2-}$ $\pi$-dimer can be described as,

$$\pi = (\chi_A + \chi_B)/\sqrt{2}$$  \hspace{1cm} (3.5)

$$\pi^* = (\chi_A - \chi_B)/\sqrt{2}$$  \hspace{1cm} (3.6)
in which the orbital overlap is dropped for simplicity of description. The covalent and ionic terms (3.1-3.3) can also be represented by MO based configurations as follows,

\[ \Psi_C = (|\pi\pi > - |\pi^*\pi^* >) /\sqrt{2} \]  
\[ \Psi_I = (|\pi\pi^* > - |\pi^*\pi^* >) /\sqrt{2} \]  
\[ \Psi_I' = (|\pi\pi > + |\pi^*\pi^* >) /\sqrt{2} \]  

(3.7)

(3.8)

(3.9)

It is also known that the ground state of a two-center bond can be represented by mixing the Hartree-Fock ground state and the doubly excited state,

\[ \Psi = d_1|\pi\pi > + d_2|\pi^*\pi^* > \]  

(3.10)

The relations between \( c_1 \) and \( d_1 \), \( c_2 \) and \( d_2 \) can be easily obtained using the above equations.\(^{14}\)

It is noted that in the above two-electron model, only the two active bonding electrons are accounted for. In \([\text{TCNE}]_2^2\) dimers, only one SOMO electron in each radical fragment is directly involved in the bonding. However, in TCNE\(^-\), there are three \( \pi \)-electrons altogether. The two \( \pi \)-electrons on the orbital below the SOMO level in each fragment do not directly participate in the formation of the dimer according to the two electron model described above (Scheme 1.1). In addition, the central CC \( \sigma \)-bonds and peripheral \( \sigma \)-bonds on each fragment are also not directly involved in the dimeric bonding. In this sense, we can view those electron pairs as nonbonding pairs, and due to the analogy with F–F, we refer these as “lone pairs”. From equation 3.4, we know that the ground state wavefunction should include a covalent part and an ionic part. Although these “lone pairs” do not directly participate the dimer bonding, they can be polarized by the bonding active \( \pi \)-electrons. For the covalent or diradical term, \( \Psi_C \), the polarization effect of these “lone pairs” can be easily accommodated by Hartree-Fock wavefunction, because the
two active electrons evenly distribute over the two centers. However for the ionic terms, $\Psi'_I$ with $A_g$ symmetry, the “lone pair” polarization effects by the + ionic structure, $A'B^+$, would be very different from the - ionic structures, $A^+B^-$, as illustrated in Scheme 3.2. This is key in the CS bonding concept. Despite, on average, the two bonding active electrons are still evenly distributed over the two fragments for the ionic terms, $\Psi'_I$, local field felt by the lone pairs should be very different when the two active electrons are A-centered or B-centered. As a result, the Hartree-Fock level is expected to approximate poorly the polarization effect by the ionic terms in the wavefunction. Even at complete active space SCF (CASSCF (2,2)) level that only includes the correlation within the bonding electrons, the “lone pair” polarization effects are not accommodated for the ionic part in the wavefunctions.

In the Hartree-Fock scheme, the ionic term, $\Psi'_I$, can be symbolically described as follows,

$$
\Psi'^{HF}_I = (|\Psi^\text{core}^n \chi_{AXA} > - |\Psi^\text{core}^n \chi_{BXB} >) / \sqrt{2},
$$

(3.11)

in which, $\Psi^\text{core}$ refers to the electrons that might be significantly polarized by the ionic structures, and we refer them as “lone pairs” in the following discussion. $\Psi^\text{core}$ refers to electrons insignificantly polarized. Here an averaged polarization effect for the nonbonding electrons is used regardless whether the two bonding electrons are on site A or site B. According to the above discussion, the ionic contribution would be underestimated at Hartree-Fock level, since the “lone pair” polarization effects are not efficiently approximated for the ionic part. The ionic contribution usually tends to enhance the bonding. As a result, the underestimated ionic contribution would lead to smaller bonding energy. One of the reasons the analogy with F-F works in this case is that TCNE is a good electron acceptor as the F atom is.

For an appropriate polarization effect, the ionic wavefunction should be in the following form,
in which the wavefunction is allowed for proper polarization when center A is doubly occupied or B is doubly occupied. Such a polarization is in effect a dynamic correlation between the lone pair electrons and the bonding electrons. At a first order approximation, the dynamic correlation effect can be seen from,

\[ \Psi^{\text{dyn}}_I = |\Psi^\text{core}_A \chi_A \bar{\chi}_A > - |\Psi^\text{core}_B \chi_B \bar{\chi}_B > \sqrt{2} \]

(3.12)

where \( \Psi^{n} \) represents the intra-pair single excitation of the lone pairs. Thus the dynamic correlation effect is invoked by a sum of double excitations, each of which contains a single excitation of a lone pair and a single excitation from the bonding pair. The correlations between the bonding pair and lone pairs would increase the ionic contribution to the bonding and hence enhance the dimer bonding due to the sensitivity of the bonding energy to the ionic contribution.

The above qualitative analysis shows the root of the dynamic correlations necessary to describe the 2e/mc bonding in \([\text{TCNE}]_2^{2-}\) dimers. Next, we show how the dynamic correlations are manifested by GVB-RCI calculations. In the above description, we have artificially classified the electrons on each fragment as nonbonding “lone pairs” and bonding active electrons. By carrying out GVB calculations, those electron pairs can be obtained as shown in Figure 3.4. In the GVB calculations, three orbitals are used for each “lone pair”. These optimized orbitals correspond to the central CC \( \sigma \)-bonds and nonbonding \( \pi \)-electrons on each fragment (Figure 3.4A and 3.4B). For the central CC \( \sigma \)-bond pairs, the double excitation to the orbital in the middle of Figure 3.4A allows left-right correlation, while the double excitation to the orbital in the right of Figure 3.4A allows for radial correlations. For the nonbonding \( \pi \)-pairs, the double
excitations to any of the two excited orbitals correspond to radial correlation. There are no left-right excitations available for these nonbonding $\pi$-pairs, because the antibonding $\pi$-orbitals (the orbitals in Figure 3.4C) along the CC bonds are used for the bonding active electron pairs. Since left-right correlation is not allowed for these pairs, two excited orbitals are used for radial correlation to guarantee sufficient room for relaxation. Two orbitals are used for the bonding active $\pi$-electrons as shown in Figure 3.4C.
**Figure 3.4.** The active orbital space for GVB-RCI calculations. A: lone pair orbitals corresponding to the $\sigma$-CC bonds; B: nonbonding $\pi$-orbitals. C: SOMO derived active orbitals active in the intermolecular bonding. The orbitals were optimized by GVB calculations.

The GVB-RCI calculations were carried out based on GVB optimized orbitals. The GVB-RCI wavefunction is symbolically described as follows,

$$
\psi^{GVB-RCI} \sim \left[ \text{core} \sum_{n=1}^{4} \left( \frac{n^2}{(n^*)^2} \right) \left( \frac{\sigma^2}{(\sigma^*)^2} \right) \right] (3.14)
$$

where for each electron pair, there are three possible configurations represented by one of the vertically stacked term. The $n$ and $\sigma$ represent the lone pairs and the bonding active electron pair based on the SOMOs of the TCNE$^-$ fragments. The notation here is only meant to show what configurations used for the RCI calculations, and does not represent the exact wavefunction. The symbols arranged vertically in 3.14 containing $n$ refer to the lone pairs, $n$, and correspond to $\psi^{*n}$ in eqn 3.13. Note that in GVB method, only the intra-pair doubly excitations are allowed, which corresponds to the intra-pair left-right correlations as shown in eq 3.15.
In GVB-RCI calculations, the coupling between two intra-pair singly excitations are additionally allowed compared to GVB method. The sum of two intra-pair singly excitations, one from a lone pair ($n$) and the other from the bonding pair ($\sigma$), corresponds a double excitation in terms of the total wavefunctions. Configuration interactions restricted in such a way are in line with the method in a previous study to demonstrate the charge shift effect in $\text{F}^{-}\text{F}$, where it shows that charge shift effect is basically dynamic correlations accounting for appropriate lone pair polarization effect by the ionic structures.

Apart from the possible charge shift effect, a qualitatively correct electronic structure should be found to account for the static electron correlation in the $[\text{TCNE}]_{2}^{2-}$ dimers. Considering the high degree of $\pi$-conjugation in those dimers, multi-configuration self-consistent field (MCSCF) method was used for this purpose. It was found that an active space including the orbitals in Figure 3.5 and corresponding electrons are necessary to obtain a qualitatively correct description of the electronic structures of TCNE anion dimers. Detailed discussions are shown in the following sections.
One top of the MCSF description, the GVB-RCI calculations were also performed. Note that in our GVB-RCI calculations, the electronic configurations were included that account for both the static correlations and the dynamic charge shift effect. Thus, the GVB-RCI configuration space actually covers both the configurations for the important resonance structures and the configurations for the intra-pair excitations as described above.

The geometry of [TCNE]$_2^{2-}$ dimer was optimized with the intra dimer distance constraint at 2.89 Å that is taken from one of the crystal structures of [TCNE]$_2^{2-}$ dimers.$^{15}$ The observed bonding distances of [TCNE]$_2^{2-}$ dimers usually fall in a range a little longer or shorter than 2.89 Å depending on the type of counter ions around the anion dimers. The M05-2X density functional was used for the constrained geometry optimization within the spin-unrestricted scheme to reflect the diradical charter of the radical dimer.

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**Figure 3.5.** The Hartree-Fock orbital space used for MCSCF calculations of [TCNE]$_2^{2-}$ with $D_{2h}$ symmetry.
The binding energies at each level were calculated by the difference between the energies associated with the separation at 2.89 Å and at 12.00 Å. Due to the negative charges on the radical fragments, the Coulomb repulsions were removed from the binding energies to obtain realistic values comparable with experiments. The change of the Coulomb repulsions were estimated by the following formula based the partial charges (Mulliken charges were used) on each atoms.

\[ E_{\text{coul}} = 14.4 \sum_{i<j} \frac{Q_i Q_j}{R_{ij}} \text{ (eV)} \]  

(3.16)

As a result, the binding energies after removal of Coulomb repulsion is expressed by,

\[ E_{\text{bind}} = (E_{2.89} - E_{\text{coul}}^{2.89}) - (E_{12.00} - E_{\text{coul}}^{12.00}) \]  

(3.17)

### 3.3 Computational details

Table 3.1 summarizes the configurations used for the calculations at different levels discussed in the following text. GVB calculations are emulated by multi-configuration self-consistent field (MCSCF) method, in which only intra-pair double excitations are allowed. As shown in Table 3.1, for each lone pair, there are three types of possible occupation because three orbitals are used for each lone pair as illustrated in Figure. 3.4 A and B. (Note that the term “lone pair” is used here for electron pairs that do not directly participate in the SOMO-SOMO bonding, but that are polarizable, as in F₂.) For the bonding active pair, there are two types of occupations. All the possible combinations of various intra-pair double excitations give overall \(3^4 \times 2^2 = 162\) configurations. Note that the GVB level contains the configurations corresponding to the
aromatic structure and diradical-I structure shown in Figure 3.6. In the following discussion, we will refer this level as Res-2 to reflect the inclusion of these two resonance structures.

As will be seen shortly in Figure 3.6, the resonance structures of aromatic, diradical-I and diradical-II, are important for static correlations of $[\text{TCNE}]_2^{2-}$. We refer to the level including all these three resonance structures as Res-3. Note that the aromatic and diradical-I structures are already included at Res-2 (or GVB) level. Therefore, to get the Res-3 level, only the two configurations corresponding to diradical-II structure are needed to be added on top of Res-2 (or GVB) level. Accordingly, there are overall 164 configurations at Res-3 level. At Res-3 level, the GVB (or Res-2) optimized orbitals were used for CI calculations by including all of the 164 configurations.

On top of the Res-3 level, we added the configurations corresponding to the intra-pair single excitations as shown in Table 3.1. It is noticed that each of the configurations are characteristic of two intra-pair single excitations: one for the bonding active pair and the other for one of the lone pairs. There is a total of 12 such configurations which are explicitly listed in Table 3.1. We refer the level as GVB-RCI by including all of the 176 configurations listed in Table 3. At GVB-RCI level, CI calculations were carried out by using the GVB-optimized orbitals with all of the 176 configurations in Table 3.1.
Table 3.1. The configurations used for the calculations at different levels discussed in the text. “n” refers to lone pairs, and “σ” refers to the SOMO-SOMO bonding active pair. (CC-σ) refers to the σ-pair in the CC bond on the ethylene unit on site A or B, and , (CC-π) refers to the π-bonding electron pair in the CC bond on the ethylene unit on site A or B. There are a total of four lone pairs in the active space. Three orbitals are used for each lone pair, and two orbitals are used for the bonding active pair. Res-2 or GVB level: 162 configurations corresponding to double intra-pair excitations are used; Res-3 level: two more configurations corresponding to diradical-II structure (See Figure 3.6) are added on top of Res-2 level; GVB-RCI: the 12 intra-pair single excited configurations are added on top of Res-3 level to get overall 176 excitations.

<table>
<thead>
<tr>
<th>Center A(CC-σ)</th>
<th>Center B(CC-σ)</th>
<th>Center A(CC-π)</th>
<th>Center B(CC-π)</th>
<th>SOMO-SOMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>n1</td>
<td>n1''</td>
<td>n2''</td>
<td>n2^*</td>
<td>n3</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

Res-2: \(3 \times 2^2 = 162\) configurations

Res-3: 164 configurations

GVB-RCI: 176 configurations
For all of the calculations, 6-31G(d) basis set was used. The basis set superposition error was corrected by counterpoise (CP) procedure. DFT calculations were performed by employing Gaussian 03 program\textsuperscript{16} and MCSCF and GVB-RCI calculations were carried out with Gamess package.\textsuperscript{17}

3.4 Results and discussion

3.4.1 MCSCF calculations and resonance structures

In the previous computational studies of 2e/mc radical $\pi$-dimers, it is usually suggested that two configurations are sufficient to qualitatively describe the electronic structures and cover the static correlation. The two corresponding configurations are defined in the active space including the HOMO and LUMO orbitals and two electrons. If the molecular system is confined within a two-electron model, such a configuration space is sufficient to statically describe the covalent and ionic characters of the bonding and the diradical charter of the dimers as demonstrated by equations 3.1-3.10. However, for $[\text{TCNE}]_2^{2-}$ $\pi$-dimers, there are six $\pi$-electrons around the two ethylene units. Of course the $\pi$-electrons on the cyano groups are also indirectly involved in the bonding, but they are irrelevant to classify the resonance structures and corresponding electronic configurations. Due to the high degree of conjugation and several $\pi$-electrons, more than two
configurations might be necessary to qualitatively describe the electronic structures related to the 2e/mc bonding in [TCNE]$_2$$^2^-$ π-dimers.

By inspecting the structure of the [TCNE]$_2$$^2^-$ dimer, we can identify three possible important resonance structures as illustrated in Figure 3.6.

![Resonance Structures](image)

**Figure 3.6.** The resonance structures with significant contributions to the 2e/mc bonding in [TCNE]$_2$$^2^-$ π-dimers. For definitions, see equations 3.18, 3.19, and 3.20.

In the aromatic structure, the two bonding active π-electrons couple not only along the CC bond in each ethylene units, but also couple across the two units. If the electron couplings (refer to “b” in Figure 3.6) across the fragmental units are blocked, a diradical structure (called biradical I) can be identified. On the other hand, if the electron couplings within each fragmental unit (refer to “a” in Figure 3.6) are broken, the biradical II structure is obtained. The electronic configurations corresponding to those resonance structures are shown in equations 3.18-3.20, where the core refers to the electrons not included in the active space defined in Figure 3.5.
relevant π–orbitals are shown in Figure 3.5, where the orbitals are denoted by the corresponding symmetry species.

\[ \Psi_{cov} = |core10b^{2}_{1u} 9b^{2}_{3u}| \]  
(3.18)

\[ \Psi_{birad I} = |core10b^{2}_{1u} 9b^{2}_{2g}| \]  
(3.19)

\[ \Psi_{birad II} = |core9b^{2}_{3u} 9b^{2}_{2g}| \]  
(3.20)

The calculated binding energies are tabulated in Table 3.2. When only the aromatic and the biradical-I structures are used, the dimer is barely bonded. By using all of the three resonance structures, a much larger binding energy is obtained. Further calculations by using the complete active space defined by Figure 3.5, there is no improvement in terms of the binding energies. Therefore, we can conclude that all of the three resonance structures are necessary to describe the electronic structure of 2e/mc bonding. This is in contrast to the previous studies\(^2\), which suggested that only two of the structures (aromatic and biradical-I) are sufficient for a qualitatively correct electronic structure description.

**Table 3.2.** The binding energies (in kcal/mol) calculated by using different number of resonance structures. Res-2: aromatic and biradical I structures; Res-3: aromatic, biradical I and II structures; CAS(6,4): all possible configurations formed by the active space defined in Figure 5.

<table>
<thead>
<tr>
<th>( E_{bind} )</th>
<th>Res-2(^a)</th>
<th>Res-3</th>
<th>CAS(6,4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.56</td>
<td>-2.95</td>
<td>-2.95</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Equivalent to CAS(2,2)
3.4.2 GVB-RCI calculations and charge shift effect

The GVB-RCI calculated binding energy is listed in Table 3.3 as well as the binding energy calculated by using all of the three resonance structures described in the above section (Denoted as Res-3 level). Note that the calculated binding energy by using three resonance structures (Res-3) is a little different from the corresponding value in Table 1. This is because the values in Table 3.2 and Table 3.3 are calculated by using Hartree-Fock orbitals and GVB orbitals, respectively.

The GVB-RCI theory level can be distinguished from the level of Res-3 in that the dynamic correlation is added on top of the Res-3, by including the configurations corresponding to the intra-pair single excitations. As discussed before, the product of two single excitations, one from the lone pairs and the other from the bonding pair provides appropriate polarization corresponding to the ionic terms as described in equations 3.1-3.13. Therefore, the charge shift effect, at this level of theory, can be defined as the difference between the binding energies at Res-3 level and that at GVB-RCI level,

\[ E_{CS} = E_{bind}^{GVB-RCI} - E_{bind}^{Res-3} \]  

(3.21)

It is noticed that at GVB-RCI level, significantly larger interaction energy is obtained compared to the Res-3 level that only covers static correlations. The charge shift contribution to the bonding defined by eq. 3.21 is 2.40 kcal/mol. Considering the small total binding energy of [TCNE]_2 \textsuperscript{2-} \pi-dimers as experimentally measured, such a charge shift contribution is significant. The binding energy at GVB-RCI level is still smaller than the experimental value. However, our study in this chapter addresses the concept of charge shift and the physical source of the dynamic
correlations in [TCNE]$_2^{2-}$ dimers, although the accurate assessment of the binding energy is itself an important issue. The underestimation of the binding energy at GVB-RCI level might arise from the fact that the electrons of the CC $\sigma$-bonds directly connected to the central ethylene units are not counted in the active orbital space. Those peripheral $\sigma$-bond pairs are also expected to affect the polarization effect for the ionic terms in the ground state wavefunction.

**Table 3.3.** The binding energies (in kcal/mol) and charge shift (CS) bonding contributions in [TCNE]$_2^{2-}$ $\pi$-dimers. The $E_{CS}$ value is only that part that is obtained at the Res-3 and GVB-RCI level, as described in the text.

<table>
<thead>
<tr>
<th></th>
<th>Res-3</th>
<th>GVB-RCI</th>
<th>Expt.$^{18}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{bind}$</td>
<td>-2.32</td>
<td>-4.72</td>
<td>-8.8</td>
</tr>
<tr>
<td>$E_{CS}$</td>
<td></td>
<td>-2.40</td>
<td></td>
</tr>
</tbody>
</table>

The influence of the charge shift effect on the bonding can also been seen from the ionic contribution to the ground state wavefunction. The ionic contribution can be characterized by the magnitude of the coefficients, $|d_1|$ and $|d_2|$ in eq 3.10. The larger the ratio of $|d_2/d_1|$, the more contribution of the ionic term to the bonding. This relationship is clearly shown by combining eqs. 3.4, 3.7, 3.8 and 3.10,

$$|c_1| = (|d_1| + |d_2|)/2$$  \hspace{1cm} (3.22)

$$|c_2| = (|d_1| - |d_2|)/2$$  \hspace{1cm} (3.23)
Smaller $|d_2/d_1|$ corresponds to larger $|c_2/c_1|$, which means larger ionic contributions in the VB description as shown by eq. 3.4.

From Table 3.4, it is noticed that the ionic contribution at GVB-RCI level is larger than that at Res-3 level, which is expected due to the dynamic correlations introduced for the ionic terms in the wavefunction. TCNE is a good electron acceptor, so the energy of ionic structure is very close to that of the diradical structures. Correspondingly, a small increase of the ionic contribution would lead to significant increase of the binding energies.

Table 3.4. The coefficients corresponding to the terms in eqs. 3.4 and 3.10.

|       | $|d_1|$ | $|d_2|$ | $|d_2/d_1|$ | $|c_1|$ | $|c_2|$ | $|c_2/c_1|$ |
|-------|-------|-------|-------------|-------|-------|-------------|
| Res-3 | 0.9182| 0.3639| 0.3963      | 0.9067| 0.3920| 0.4323      |
| GVB-RCI| 0.9213| 0.3465| 0.3761      | 0.8966| 0.4065| 0.4534      |

3.5 Conclusions

By using MCSCF calculations, three resonance structures are identified, which are necessary for a qualitatively correct description of the electron structure of the 2e/mc bonding of $[\text{TCNE}]_2^{2-}$-dimers. We found that all of the three structures should be used to cover the static correlations for the 2e/mc bonding. This is in contrast to the previous studies that suggest only aromatic and diradical I structures are sufficient for a qualitative description of those radical $\pi$-dimers. A significant charge shift contribution to the 2e/mc bonding was found. By using GVB-RCI calculations, we show that the physical nature of the charge shift effect arises from the correlations between the bonding pairs and the nonbonding pairs. Such inter-pair correlations are
realized in GVB-RCI calculations by the double excitations, which correspond to two intra-pair single excitations from two different pairs, one from the lone pairs and the other from the bonding pair. Hence, the lone pair or the nonbonding pairs are allowed to properly be polarized by the ionic terms in the total wavefunctions, which is indicated by the increased ratio of $|c_2/c_1|$. Our investigations manifested that the covalency of 2c/mc bonding systems is analogous to that of F–F, which can be broadly defined as covalent bond but with significant charge shift effect.

References


CHAPTER 4

FLUXIONAL $\sigma$-BONDS OF 2,5,8-TRI-TERT-BUTYL-1,3-DIAZAPHENALENYL DIMERS: STEPWISE [3,3], [5,5] AND [7,7] SIGMATROPIC REARRANGEMENTS VIA $\pi$-DIMER INTERMEDIATES

4.1 Introduction

Phenalenyl 1 is a stable odd alternant hydrocarbon radical that undergoes $\sigma$-dimerization in solution as depicted in Scheme 4.1. A number of phenalenyl derivatives form $\pi$-dimers and $\pi$-stacks, which have attracted much attention due to their interesting electronic, optical and magnetic properties. One of the isolated phenalenyl $\pi$-dimers is shown in Chart 4.1, where the bulky tert-butyl groups prevent the $\sigma$-dimerization.

**Scheme 4.1.** $\sigma$-Dimerization of phenalenyl radical.

---

Chart 4.1. The structure of the 2,5,8-tri-tert-butyl-phenalenyl radical (3), the π-dimer (4), and the simplified π-dimer model system (5) obtained by replacing the tert-butyl groups of 4 with hydrogens (not shown).

Phenalene 6, the hydrogenated phenalenyl, undergoes six-fold valence tautomerization (Scheme 4.2) owing to the hydrogen shift of the benzylic-allylic hydrogen, according to NMR evidence. Inspired by these phenomena, we proposed that the phenalenyl σ-dimers undergo six-fold sigmatropic rearrangements by breaking and forming the inter-phenalenyl CC σ-bond that is the counterpart of the C(sp³)–H bond in phenalene. However, such σ-bond shift has not been observed because most of the experimentally isolated phenalenyl derivatives exist in the form of π-dimeric structures.

Scheme 4.2. The chemical structure of phenalene (6) and the schematic six-fold hydrogen transfer process.
The title compound, 2,5,8-tri-tert-butyl-1,3-diazaphenalenyl radical (DAzPh) 7 (Chart 4.2), is a substituted analogue of phenalenyl. Direct evidence from X-ray diffraction and UV-vis spectroscopy indicates\(^7\) that the radicals are stabilized by forming $\sigma$-dimers 8 (Chart 4.2) in a staggered cofacial stacking pattern owing to the steric repulsions of the bulky tert-butyl groups at the three $\beta$-positions. The observed contact distance is too long for a $\sigma$-bond and too short for a van der Waals (vdW) contact at 2.153 Å.\(^7\) The steric repulsion of the bulky tert-butyl groups in 8 hinders the flexible rotation about the inter-phenalenyl C–C bond, which on the other hand keeps the two DAzPh units in proximity. We propose that the $\sigma$-dimer 8 has the possibility to undergo multi-faceted $\sigma$-bond shifts. Scheme 4.3 illustrates how a [5,5] sigmatropic rearrangement to an energetically degenerate structure $8'$ might occur as the C7–C22 bond migrates to C3–C16. Note, that the ordinary terminology of [n,m] sigmatropic rearrangements is somewhat ambiguous in this case, given the delocalized $\pi$-electron network of the phenalenyl derivatives undergoing the rearrangement. We follow the shortest path in defining n and m.

**Chart 4.2.** The schematic structures of DAzPh (7) and DAzPh $\sigma$-dimer (8).
Scheme 4.3. Schematic of a σ-bond shift of 9. *tert*-butyl groups and hydrogen atoms are omitted for clarity. Structure 9 represents the π-dimeric form of the title dimer. The gray atoms are nitrogen. It will be shown to be a stable π-dimer, not a transition state.

Compared to the H-shift of phenalene, the prominent feature of the possible σ-bond transfer of DAzPh σ-dimer is that the transition structures (TS) or intermediate structures connecting the valence tautomers might be stabilized possibly by the singly occupied molecular orbital interactions (SOMO-SOMO) upon the σ-bond cleavage. Such a 2 electron multicenter (2e/mc) bonding in the π-dimer has attracted much attention recently. Therefore, we were intrigued whether the barriers to the various interconversions of the valence tautomers of the title compound are sufficiently low for fluxional σ-bonding. In this chapter, we present a computational study of the DAzPh σ-dimer rearrangement by exploring the potential energy surface (PES) of its multiple valence tautomerization pathways. The structural, electronic and magnetic properties are investigated to elucidate the nature of different dimer structures. Additionally, new valence tautomeric dimer structures are also predicted.
4.2 Computational Methods

In the process of the C–C bond migration of the σ-dimer from 8 to 8', the extreme structure upon the cleavage of the inter-phenalenyl CC bond is a SOMO-SOMO bonded π-dimer. In principle, there are 26 electrons involved in the bond-breaking and bond-forming process owing to the relative high conjugation of the DAzPh rings. In other words, the π-MOs change drastically during the change from a π-dimer (2×13=26 π-electrons) to a σ-dimer (2σ + 24 π-electrons). Multireference based descriptions including all the active electrons would be desirable but are computationally difficult. In the following section we describe our selection of a DFT method that performs consistently with respect to the reactant and the TS (or intermediate) structures so as to yield quantitatively or at least qualitatively correct potential energy profiles along the reaction path.

Two DFT methods were employed for our calculations: the hybrid meta-generalized gradient M05-2X functional, and Becke’s three parameter hybrid exchange functional in combination with Lee-Yang-Parr correlation functional (B3LYP). The broken-symmetry (BS) spin-unrestricted DFT scheme was used whenever a solution with a lower energy can be found than in the spin-restricted scheme. This is indicated by the prefix U throughout. The potential energy surface (PES) was explored by relaxed scans along the inter-phenalenyl separation. Unless stated otherwise, all geometries were optimized with UM05-2X/6-31G(d,p), and in some cases single point energies were also calculated with the 6-311+G(2d,p) basis set based on the optimized geometries. For the binding energy calculations of the π-dimers, the basis set superposition error (BSSE) was corrected by the counterpoise method. As shown in the next section, the UM05-2X method correctly describes the dissociation of the parent phenalenyl π-dimer 4 yielding binding
energy and inter-phenalenyl separation in good agreement with experiments. Therefore, we employed UM05-2X to investigate the \( \sigma \)-bond rearrangement of the DAzPh dimer and its various valence tautomers. Vibrational frequency analyses were carried out at each stationary point to identify the nature as a minimum or a transition state. The adiabatic excitation energies and the singlet-triplet gaps (\( \Delta E_{\text{st}} \)) of the \( \pi \)-dimers were calculated at (2,2)CASPT2\(^{12}\)/cc-pVDZ level with the optimized geometries of the ground singlet state obtained by UM05-2X method. The natural orbitals (NO) and their occupation number of the broken symmetry DFT solutions were obtained by diagonalizing the one electron density matrices. All DFT calculations were performed with Gaussian03.\(^{13}\) CASPT2 calculations were carried out applying Molpro 2006.1.\(^{14}\)

To eliminate spin contamination of the BS solutions, the total energies of low spin states of the \( \pi \)-dimers were estimated by using the approximate spin projection (AP) procedure as described by the following equation.\(^{15}\)

\[
E_{\text{AP-LS}} = E_{\text{LS}} + J_{ab}(AP) \times [\langle S^2 \rangle_S - S_{\text{min}} (S_{\text{min}} + 1)],
\]

(4.1)

where \( E_{\text{LS}} \) and \( \langle S^2 \rangle_{\text{LS}} \) are the total energy and spin angular momentum of low spin state (LS), respectively; \( S_{\text{min}} \) is the spin angular momentum of the pure LS state; \( J_{ab}(AP) \) is the effective exchange integral calculated by,

\[
J_{ab} = \frac{E_{\text{LS}} - E_{\text{HS}}}{\langle S^2 \rangle_{\text{LS}} - \langle S^2 \rangle_{\text{HS}}},
\]

(4.2)

where \( E_{\text{HS}} \) and \( \langle S^2 \rangle_{\text{HS}} \) are the total energy and spin angular momentum of low spin state (LS), respectively.
4.3 Validation of the DFT methods

As we examined in the next section, the cleavage of the inter-phenalenyl C–C bond in 8 gives rise to π-dimer intermediates 9. It is expected that the calculations about this π-dimer would be the most challenging part on the potential energy profile due to the weak bonding at vdW range. The electronic structure of 9 is in essence similar to that of the 2,5,8-tri-tert-butyl-phenalenyl π-dimer, 4 (Chart 4.1), in the sense that both of them are singlet diradicaloids. Recent work emphasized the role of vdW interactions in the formation of the multicenter bonding in these and similar systems. The structure and physical properties of 4 have been well documented in the literature both experimentally and theoretically. Therefore, we used 4 as a reference system to evaluate the computational methods.

We first calculated the binding energy surface \( E_{\text{bind}} = E_{\text{tot}}(\text{dimer}) - 2E_{\text{tot}}(\text{monomer}) \) of the π-dimer 4 as a function of the inter-phenalenyl separation. To simplify the calculations of the PES, we replaced the tert-butyl groups by hydrogens as shown by 5 in Chart 4.1. The geometries at each separation were optimized with 6-31+G(d,p) basis set by fixing the central C-C distances. As suggested in previous studies, restricted DFT scheme is generally unstable with respect to the unrestricted method since the latter gives qualitatively correct wavefunctions by including static correlation arising from the diradicaloid nature of the phenalenyl π-dimers. Therefore, we only show the calculated results by the unrestricted method using UB3LYP and UM05-2X, which produce lower energy solutions compared to the corresponding restricted DFT at larger R values where the electronic state becomes diradicaloid. As shown in Figure 4.1, UB3LYP calculations are incorrect as the PES of the two phenalenyl units is overall repulsive. For multicenter π-bonding systems, like phenalenyl and \([\text{TCNE}]_2^{2-}\) π-dimers, it is believed that the
SOMO-SOMO binding interactions contribute to stabilizing the $\pi$-dimer. However, alone they are insufficient to overcome the exchange and Coulomb repulsions.\textsuperscript{19} vdW interactions are essential for the overall binding.\textsuperscript{20} Although the UB3LYP method includes part of the static correlation by allowing to “localize” the $\alpha$ and $\beta$ bonding orbitals, long range dynamic correlation essential for vdW attraction is missing. In contrast to UB3LYP, UM05-2X shows a reasonable dissociation curve with an overall attractive binding for the $\pi$-dimer. The minimum at 3.161 Å is in good agreement with 3.200 Å of X-ray structure of $4^4$ and with 3.1 Å obtained by PP(1)-MP2 calculations\textsuperscript{16a} on the simplified $\pi$-dimer model (5). The UM05-2X curve starts to show a broken symmetry (BS) solution when the central CC separation is longer (or equal to) than 3.00 Å. For the UB3LYP, BS appears at 3.20 Å. Both methods indicate therefore a biradicaloid state at large separations, but only UM05-2X has the right dissociation energetics with overall attractive binding at the equilibrium distance.

![Figure 4.1](image_url)

**Figure 4.1.** The binding energy surface of the simplified phenalenyl $\pi$-dimer (5) as a function of the inter-phenalenyl separation $R$ defined by the central C-C distance. BSSE and ZPE correction are not included. For method description, see text.
In Table 4.1, note the sudden rise of $<S^2>$ when the separation changes from 3.4 Å to 3.6 Å. This sudden rise is related to the small discontinuity of the energy curve at 3.40 Å in Figure 4.1.

**Table 4.1.** The $<S^2>$ of $\pi$-dimer 4 for part of geometries on the potential surface calculated by UB3LYP/6-31+G(d,p).

<table>
<thead>
<tr>
<th>Separation (in Å)</th>
<th>3.00</th>
<th>3.20</th>
<th>3.40</th>
<th>3.60</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt;S^2&gt;$</td>
<td>0.0000</td>
<td>0.2466</td>
<td>0.3936</td>
<td>1.0135</td>
</tr>
</tbody>
</table>

The UM05-2X calculated binding energies with counterpoise (CP) and zero point energy (ZPE) corrections are listed in Table 4.2 in comparison with the experimental values and the calculated values by PP(1)-MP2.\(^{21}\) To make the calculations more realistic, we also calculated the binding energy using the tert-butyl substituted phenalenyl $\pi$-dimer (4). The calculated intermolecular distance for 4 is 3.209 Å which is very close to the X-ray value of 3.200 Å.\(^4\) The UM05-2X calculated binding energy after CP and ZPE correction, -7.96 kcal/mol, is also very close to the available experimental values of binding energy.\(^{16}\) We attribute the good performance of the UM05-2X method to two reasons. First, the diradicaloid character of the $\pi$-dimer can be treated by unrestricted DFT calculations with a single-determinant scheme.\(^{22}\) Second, M05-2X performs well for $\pi-\pi$ stacking interactions with vdW interactions.\(^{23}\)
Table 4.2. Optimized Inter-Phenalenyl Central C-C Separations (R in Å) and Binding Energies (∆E in kcal/mol) of 4 and 5 Compared with Experiments

<table>
<thead>
<tr>
<th>Properties</th>
<th>6-31+G(d,p)</th>
<th>6-311+G(2d,p)</th>
<th>PP(1)-MP2</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3.209</td>
<td>-</td>
<td>-</td>
<td>3.20</td>
</tr>
<tr>
<td>5</td>
<td>3.161</td>
<td>-</td>
<td>3.1</td>
<td>-</td>
</tr>
<tr>
<td>∆E</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>-7.77</td>
<td>-7.96</td>
<td>-</td>
<td>-7.50, -8.80, -9.50</td>
</tr>
<tr>
<td>5</td>
<td>-7.07</td>
<td>-7.87</td>
<td>-11.0</td>
<td></td>
</tr>
</tbody>
</table>

a Single point energy at the 6-31+G(d,p) optimized geometries.

b Ref 4.

c Reference 16a.

d BSSE and ZPE corrected results; the ZPE correction is calculated by UM05-2X/6-31G(d,p)//UM05-2X/6-31G(d,p).

e UV-vis, ref. 16b.

f UV-vis, ref. 16a.

g ESR, ref. 16a.

h Not corrected by ZPE.

4.4 Rearrangement of the DAzPh σ-dimer, 8

In this section, the discussion is based on the dimeric structures with staggered cofacial stacking pattern observed by X-ray diffraction for 8.7a The Newman projection of the dimeric structures is shown in Chart 4.3, where one NN, two NC and three CC pairs are in close face-to-face contacts. The dipole moments of the two DAzPh units cross at a 60° angle. We denote this staggered cofacial stacking pattern as the “crossing arrangement” to distinguish it from the anti-
parallel cofacial arrangement of the dipoles to be discussed in the next section. Accordingly, all
the dimeric structures corresponding to the crossing dipoles are denoted by a prefix “cross”.

**Chart 4.3.** Newman projection along the central carbons of the DAzPh *cross*-σ-dimer (8),
which in this projection looks identical to the *cross*-π-dimer (9). Arrows indicate the molecular
dipoles. Atoms in parenthesis belong to the distal monomer.

Figure 4.2 and Table 4.3 summarizes the main results of the UM05-2X calculations. The
optimized inter-phenalenyl σ-bond of the reactant 8 is longer than normal CC single bonds but
significantly shorter than the longest observed C-C σ-bond. During the rearrangement process,
the C7-C22 σ-bond is broken as shown in Figure 4.2. A transition structure of *cross*-TS-1 (10)
was located with a bond distance of 2.468 Å. With further increase of the C7-C22 distance, a
*cross*-π-dimer intermediate (9) was identified that has *C*₂ symmetry apart from the *tert*-butyl
substituents. The activation barrier on the reactant side is 10.21 kcal/mol. This relatively low
activation energy is mainly due to the aromatic stabilization energy achieved by each phenalenyl
unit when the C7-C22 bond is broken. After ZPE and spin contamination correction, the *cross*-π-
dimer intermediate (9) is higher in energy by only 1.33 kcal/mol compared to the reactant of cross-σ-1 dimer (8), in close agreement with the experimental value of 2.62 kcal/mol.\textsuperscript{7c} Since the experimental value was obtained by optical absorption in solid state, the conversion from cross-σ-1 dimer 8 to cross-π-dimer 9 may be hindered by crystal packing.

**Figure 4.2.** The σ-bond cleavage process of the cross-σ-1 dimer (8). The tert-butyl groups and hydrogen atoms are omitted in the drawing for clarity. The bond distances are in angstroms. Grey represent carbon.
Table 4.3. Relative Stability and Geometry Parameters of the Stationary Points on the Potential Surface of 8 and its Valence Tautomers.

<table>
<thead>
<tr>
<th>Stationary Point</th>
<th>UM05-2X/6-31G(d,p)</th>
<th>UM05-2X/6-311+G(2d,p)</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R (^{b})</td>
<td>(\Delta E (^{c})</td>
<td>(\Delta E_{ZPE} (^{c})</td>
</tr>
<tr>
<td>cross-(\sigma)-1, 8</td>
<td>1.633</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>cross-TS-1, 10</td>
<td>2.468</td>
<td>11.96</td>
<td>9.91</td>
</tr>
<tr>
<td>cross-(\sigma)-2, 12</td>
<td>1.636</td>
<td>1.50</td>
<td>1.74</td>
</tr>
<tr>
<td>cross-TS-2, 11</td>
<td>2.382</td>
<td>11.76</td>
<td>9.79</td>
</tr>
<tr>
<td>cross-(\sigma)-3, 13</td>
<td>1.538</td>
<td>12.24</td>
<td>-</td>
</tr>
<tr>
<td>cross-(\sigma)-4, 14</td>
<td>1.505</td>
<td>37.17</td>
<td>-</td>
</tr>
<tr>
<td>cross-(\pi), 9</td>
<td>3.274</td>
<td>5.28</td>
<td>1.76</td>
</tr>
</tbody>
</table>

\(^{a}\) Single point energy at the 6-31+G(d,p) optimized geometries.

\(^{b}\) \(R\) is the C7-C22 distance in Å for 8, 9, and 10; C5-C24 distance for 11 and 12; C18-N2 or C9-N19 distance for 13; N1-N14 distance for 14.

\(^{c}\) \(\Delta E\) and \(\Delta E_{ZPE}\) are the energies before and after ZPE corrections (in kcal/mol). The cross-\(\sigma\)-1 (8) is used as the reference energy. The ZPE correction is calculated by UM05-2X/6-31G(d,p)//UM05-2X/6-31G(d,p).

\(^{d}\) This is the second shortest CC contact. The shortest is C13-C26 =3.238 Å.

\(^{e}\) The number in parenthesis is the relative energy without the spin contamination correction by the AP procedure. \(^{f}\) Spin correction is included. \(^{g}\) Reference 4c.

Due to the small energy difference, the \(\pi\)-dimer intermediate 9 is thermally accessible even though \(\sigma\)-dimer 8 is the global minimum. This is consistent with the disorder of the crystal structure at room temperature (R=15%) leading to an apparent intermolecular C7-C22 distance.
of 2.153 Å. Our results confirm the interpretation that the 2.153 Å C7-C22 contact distance is close to the population weighted average of 2.242 Å between the σ-dimer 8 and π-dimer 9. It is noted that the refinement of the crystal structures was just based on the structure of 8 and 9. However, according to our calculations, the three valence tautomers 8, 9 and 12 are thermally accessible. That might be the reason that the calculated average C7-C22 distance is larger than the X-ray value of 2.153 Å, because the C7-C22 distance would have more probability to stay at larger separation when the valence tautomer 12 is included in the averaging.

Upon the formation of the cross-π-dimer intermediate 9, there are four possible exit channels to form inter-phenalenyl σ-bonds as depicted in Figure 4.3. Owing to the bulky tert-butyl groups, the two phenalenyl units are confined to a staggered π-stacking geometry. There are six pairs of active atoms that are in close face-to-face contact. Correspondingly, six σ-dimers can be identified when these atom pairs get close leading to σ-bonds. Because of the $C_2$ symmetry of the cross-π-dimer 9, two pairs of the σ-dimers are degenerate structures, cross-σ-1(cross-σ-1’) (8 and 8’) and cross-σ-3(cross-σ-3’) (13 and 13’). Therefore, four distinct σ-dimers were found by the calculations after the rearrangement of the σ-dimer reactant 8 as shown in Figure 4.3. Accordingly, four transition structures exist connecting the π-dimer and each σ-dimer. The corresponding energetics and inter-phenalenyl bonds distances are summarized in Table 4.3. Among the four kinds of σ-dimers, the electronic energy of cross-σ-3(cross-σ-3’) (13) and cross-σ-4 (14) are substantially higher than the π-dimer intermediate, which is consistent with the fact that C-N and N-N bonds are weaker than C-C bonds. Therefore, the two corresponding rearrangements are not favored, and we will focus on the reaction pathway corresponding to
cross-σ-1' (8') and cross-σ-2 (12). The two transition structures deemed to be high in energy leading to 13 and 14 are omitted from the investigation.

Figure 4.3 Four channels (UM05-2X/6-31G(d,p) level.) of the σ-dimerization of the title dimer starting from the π-dimer intermediate 9. Hydrogens are not shown. TS indicates transitions states, which are only indicated for the low energy channels. For energies, see Table 4.3.

The σ-bond shift from cross-σ-1 (8) to cross-σ-1' (8') corresponds to a stepwise degenerate [5,5] sigmatropic rearrangement via 9 as the intermediate. The relaxed electronic PES is shown in Figure 4.4, in which the intermolecular C7-C22 and C3-C16 distances are used as the reaction coordinates. On the PES, the cross-π-dimer intermediate 9 with C2 symmetry is separated from the symmetric flanking structures cross-σ-1 (8) and cross-σ-1' (8') by a 3.10 kcal/mol barrier. The electronic structure is diradicaloid only in the vicinity of 9 on the PES given in Figure 4.4.
**Figure 4.4.** Relaxed PES of the *cross*-σ-1 dimer calculated by UM05-2X/6-31G(d,p) along the C7-C22 distance (the left half) and the C3-C16 distance (the right half). The AP and ZPE corrections are indicated only for 9 and are relative to the respective values for 8. The curve is presented to guide the eye. The reduction of the energy difference due to ZPE is given in more detail in Table 4.3.

The inter-phenalenyl C7-C22 distance of 3.274 Å in the π-intermediate 9 suggests that the rearrangement proceeds through a stepwise dissociative process, which is in contrast to the stepwise associative process via the bis-allyl diradical intermediate for the [5,5] sigmatropic rearrangement of 5,5a,10,10a-tetrahydroheptalene.\(^{25}\) Furthermore the energy difference between σ-dimer 8 and the π-dimer intermediate 9 is only 1.33 kcal/mol after ZPE and BSSE corrections, much lower than 23.9 kcal/mol for the rearrangement of 5,5a,10,10a-tetrahydroheptalene.
In addition to the degenerate [5,5] rearrangement, the σ-bond shift from C7-C22 (or C2-C16) to C5-C24 corresponds to a nondegenerate [3,3] rearrangement. Cross-σ-2 (12) is 1.85 kcal/mol higher in energy than cross-σ-1 (8'). Therefore, the nondegenerate [3,3] rearrangement is energetically less favored than the [5,5] rearrangement. The inter-phenalenyl σ-bonds in 8 are anticipated to be very fluxional with easy interconversion between 8 and 8' due to the low barrier.

4.5 New predicted dimeric structures with anti-parallel cofacial stacking pattern

In the previous section, all the dimeric structures are based on the crossing cofacial arrangement of the monomer dipole moments, which has been observed by X-ray diffraction. After 120° rotation of one phenalenyl unit relative to the other, the dipoles are oriented antiparallel, and a new staggered cofacial arrangement with four pairs of CN and two pairs of CC contacts are obtained. The corresponding Newman projection is shown in Chart 4.4.

Chart 4.4. The Newman projection taken along the two central carbons of the predicted anti-dimeric structures. Arrows indicate the molecular dipoles. Atoms in parenthesis belong to the distal monomer.
This stacking arrangement is denoted by the “anti” prefix. None of the anti dimer structures have been observed yet. Our calculations indentified the two-fold degenerate anti-σ-1 dimers (15) and the four-fold degenerate anti-σ-2 dimers (16), and one anti-π-dimer (17) as shown in Figure 4.5 and Figure 4.6 as local minima on the PES. The energy differences at our level of theory are less than 2 kcal/mol between the cross-σ-1 dimer (8) and the anti-σ-1 dimer (16), or between the cross-π-dimer (9) and the anti-π dimer (17) (See Table 4.4). Therefore, we anticipate that the anti-parallel dimeric structures are likely to be isolated under suitable conditions.

![Figure 4.5](https://example.com/figure45.png)

**Figure 4.5.** Relaxed PES of the anti-σ-1 dimer 15 calculated by UM05-2X/6-31G(d,p) along the C2-C18 distance (the left half) and the C7-C22 distance (the right half). See Figure 4.6 for the atom numbering.
Figure 4.6. The structures of the anti-σ-dimers and anti-π-dimer calculated at UM05-2X/6-31G(d,p) level. tert-butyl groups and hydrogen atoms are neglected in the drawing for clarity. The labeled bond distances are in angstroms. Blue represents nitrogen and grey represents carbon.

Table 4.4. The total and relative energies (a. u.) of the dimers with cross and anti-parallel dipole arrangement.

<table>
<thead>
<tr>
<th>Basis set</th>
<th>$\text{cross-σ-1 (8)}$</th>
<th>$\text{anti-σ-1 (15)}$</th>
<th>difference</th>
<th>$\text{cross-π (9)}$</th>
<th>$\text{anti-π (17)}$</th>
<th>difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-311+G(2d,p)</td>
<td>-2009.6809</td>
<td>-2009.6780</td>
<td>-0.0029</td>
<td>-2009.6665</td>
<td>-2009.6671</td>
<td>0.0006</td>
</tr>
</tbody>
</table>

Next we explored the rearrangement of the predicted anti-σ-dimers. The energetics of the dimers are listed in Table 4.5. The C-C anti-σ-dimer (15) is much more stable than the C-N bonded anti-σ-dimer (16), which therefore will not be discussed. Similar to the rearrangement of the cross-σ-dimer (8), the relaxed PES (See Figure 4.5) of 15 contains a $C_{2h}$ anti-π-dimer
intermediate (17). The energy of the anti-σ-1 (15) is lower by 0.77 kcal/mol than that of the anti-π dimer (17). Starting from the π-dimer intermediate, an inter-phenalenyl σ-bond forms again leading to anti-σ-1' (15') identical to 15. The barrier on the reactant side is 11.14 kcal/mol, which is very close to the barrier for the sigmatropic rearrangement of cross-σ-dimer (8). The low reaction barrier suggests that the σ-bond in the predicted dimer 15 is also fluxional, and can easily shift from C2-C18 to C7-C22 corresponding to a degenerate stepwise [7,7] sigmatropic rearrangement proceeding via a π-dimer stabilized by SOMO-SOMO bonding.

Table 4.5. Relative Stability and Geometry Parameters of the Stationary Points on the Potential Energy Surface of 15 and its Valence Tautomers.

<table>
<thead>
<tr>
<th></th>
<th>UM05-2X/6-31G(d,p)</th>
<th>UM05-2X/6-311+G(2d,p)²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R⁵</td>
<td>ΔE⁶</td>
</tr>
<tr>
<td>anti-σ-1, 15</td>
<td>1.631</td>
<td>0</td>
</tr>
<tr>
<td>anti-TS-1, 18</td>
<td>2.510</td>
<td>12.21</td>
</tr>
<tr>
<td>anti-σ-2, 16</td>
<td>1.547</td>
<td>9.18</td>
</tr>
<tr>
<td>anti-π, 17</td>
<td>3.292</td>
<td>5.30</td>
</tr>
</tbody>
</table>

²Single point energy at the 6-31+G(d,p) optimized geometries.

R is the C2-C18 distance (Å) for 15 and 18; C1-N14 distance for 16; C13-C26 distance for 17.

ΔE and ΔE_{ZPE} are the energies (in kcal/mol) before and after ZPE corrections, respectively. The anti-σ-1 (15) is the reference energy. The ZPE correction is calculated by UM05-2X/6-31G(d,p)//UM05-2X/6-31G(d,p).

With AP corrections included.
4.6 Electronic structures

The paramagnetic susceptibilities are closely related to the electronic structures of the \( \pi \)-dimer intermediates. In this section, we aim to estimate how the hetero nitrogen atoms and dimeric stacking pattern influence the electronic structure and the magnetic properties of the DAzPh dimers.

Temperature dependent susceptibility data\(^{26}\) show strong antiferromagnetism for 4. DFT calculations\(^{27}\) suggest that the SOMO-SOMO overlap plays a crucial role in the antiferromagnetic coupling strength, and consequently affects the magnetic properties and the stability of the \( \pi \)-dimers. The SOMO-SOMO splitting can be estimated by the highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO-LUMO) gaps of the restricted closed shell calculations, with larger HOMO-LUMO gaps indicative of larger SOMO-SOMO splittings (the excitation energy at CASPT2 level are discussed below). As shown in Table 4.6, the phenalenyl \( \pi \)-dimer (4) has a larger HOMO-LUMO gap than the cross-\( \pi \)-dimer (9), which is consistent with the experimental trend seen in the UV-vis absorbance. The predicted anti-\( \pi \)-dimer 17 has an even smaller gap than the cross-\( \pi \)-dimer 9. The energy gaps corresponding to the HOMO-LUMO excitation were calculated at the (2,2)CASPT2 level. The calculated excitation energies are in good agreement with experiments, and indicate the same trend that the predicted anti-\( \pi \)-dimer 17 has the smallest excitation energy of the three phenalenyl \( \pi \)-dimers covered in this chapter. A natural orbital analysis was also carried out for these \( \pi \)-dimers and the corresponding occupation numbers of the LUMO are also listed in Table 4.6.
**Table 4.6. Calculated Structural and Electronic Parameters of Three π-Dimers**

<table>
<thead>
<tr>
<th></th>
<th>$R$ (Å)</th>
<th>Occ.</th>
<th>$E_{\text{CASPT2}}$</th>
<th>$E_{H-L}$</th>
<th>$\lambda_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>3.209</td>
<td>0.42</td>
<td>598</td>
<td>420</td>
<td>595$^c$</td>
</tr>
<tr>
<td>9</td>
<td>3.238</td>
<td>0.53</td>
<td>637</td>
<td>443</td>
<td>670$^d$</td>
</tr>
<tr>
<td>17</td>
<td>3.292</td>
<td>0.60</td>
<td>667</td>
<td>470</td>
<td>N/A</td>
</tr>
</tbody>
</table>

$^a$ $R$ is the inter-phenalenyl separation at the central carbons (Å); Occ. is the occupation number of the LUMO; $E_{\text{CASPT2}}$ is vertical excitation energies calculated by (2,2)CASPT2; $E_{H-L}$ is the HOMO-LUMO gap; $\lambda_{\text{max}}$ corresponds to the UV-vis absorption peak.

$^b$ The tert-butyl groups in 4, 9 and 17 are replaced with hydrogens to simplify the calculations.

$^c$ Reference 16a.

$^d$ Reference 7c.

The order of the LUMO occupation numbers is consistent with the SOMO-SOMO splittings. We attribute the relatively smaller splittings obtained for the 9 and 17 to the depletion of HOMO electron density on the nitrogen sites as shown by the SOMO diagram of the DAzPh (7) radical in Chart 4.5. In contrast, for the parent phenalenyl radical (3) the HOMO electrons are evenly distributed among the active carbon sites.\(^{28}\) The less evenly distributed SOMO is less favorable for the dimer orbital overlap.\(^{29}\) The anti-π-dimer 17 shows smaller splitting than the cross-π-dimer 9 because there are more CN contacts in the former.
Chart 4.5. The SOMO diagram of DAZPh (7).

Based on the smaller SOMO-SOMO splitting of anti-\(\pi\)-dimer (17) than the cross-\(\pi\)-dimer 9, it is expected that the binding energy\(^{30}\) of 17 should be smaller in magnitude than 9, as discussed with respect to data in Table 4.6. However, our calculations indicate that 17 has a larger magnitude of binding energy than the cross-\(\pi\)-dimer (9) as shown in Table 4.7. This arises from the different strength of the dipole-dipole interactions of the two \(\pi\)-dimeric systems, the dipole-dipole interaction being attractive for the anti and slightly repulsive for the cross tautomer. One notes from Chart 4.3 that for cross-\(\pi\)-dimer 9, the two dipole moments of each phenalenyl units cross with an angle of 60°, which leads to a repulsive dipole-dipole interaction. For the anti-\(\pi\)-dimer 17 as shown in Chart 4.4, the two dipole moments are anti-parallel resulting in an attractive dipole-dipole interaction. The dipole-dipole interaction energy can be estimated by equation (4.3),

\[
E_{d-d} = \frac{N}{4\pi\varepsilon_0 R^3} \left\{ \frac{\mathbf{\mu}_A \cdot \mathbf{\mu}_B - 3(\mathbf{\mu}_A \cdot \mathbf{R})(\mathbf{\mu}_B \cdot \mathbf{R})}{R^2} \right\}
\]

where \(N\) is Avogadro’s constant, \(\varepsilon_0\) is vacuum permittivity, \(R\) is the distance of the mass centers of the two phenalenyl units, \(\mu_A\) and \(\mu_B\) are the dipole moments. In this case \(\mu_A = \mu_B = 3.839\) D = 73
12.8*10^{30} \text{ (Cm)} \text{ as obtained by UM05-2X/6-31G(d,p). Upon the elimination of the dipole-dipole contributions to the binding energies, we found that the cross-$\pi$-dimer 9 shows larger estimated remainder binding energy than the anti-$\pi$-dimer 17 as given in the last column of Table 4.7. The closeness of the binding energy values of the cross- and anti-$\pi$-dimers provides further evidence that at least in solution both should be present and therefore the anti-form should be isolable.}

**Table 4.7.** The Binding Energy (kcal/mol) of the cross-$\pi$-Dimer (9) and the anti-$\pi$-Dimer (17) Calculated by UM05-2X/6-31G(d,p) and Corrected by BSSE. $E_{bind}$ and $E_{bind}^{d-d}$ are the Binding Energies Before and After the Elimination of the Classical Dipole-Dipole Contribution, $E_{d-d}$

<table>
<thead>
<tr>
<th></th>
<th>$E_{bind}$</th>
<th>$E_{d-d}$</th>
<th>$E_{bind}^{d-d}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cross-$\pi$, 9</td>
<td>-10.81</td>
<td>0.49</td>
<td>-11.3</td>
</tr>
<tr>
<td>anti-$\pi$, 17</td>
<td>-11.09</td>
<td>-0.99</td>
<td>-10.1</td>
</tr>
</tbody>
</table>

**4.7 Paramagnetic susceptibility of the $\pi$-dimer intermediates**

Table 4.8 summarizes the calculated $\Delta E_{st}=E_S-E_T$ values needed for the magnetic susceptibility calculations. The calculated $\Delta E_{st}$ of -6.80 kcal/mol for 4 is in good agreement with the experiment value of -6.64 kcal/mol.\textsuperscript{7c} The calculations indicate that 9 and 17 have a smaller magnitude for $\Delta E_{st}$ than 4, which is consistent with the larger SOMO-SOMO splittings for the latter case.
Because of the coexistence of the $\sigma$-dimers and $\pi$-dimers due to fluxional bonding, modified Bleaney-Bowers formulas\textsuperscript{31} were used for the paramagnetic susceptibility calculations.

**Table 4.8.** Estimated Relative Energy (in kcal/mol) Corresponding to Scheme 4.4

<table>
<thead>
<tr>
<th></th>
<th>4</th>
<th>9</th>
<th>17</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_1$ ($\Delta E_{st}$)\textsuperscript{a}</td>
<td>-6.80 (-6.64)\textsuperscript{b}</td>
<td>-4.19</td>
<td>-4.94</td>
</tr>
<tr>
<td>$J_2$</td>
<td>-</td>
<td>-3.67</td>
<td>-5.71</td>
</tr>
<tr>
<td>$J_3$</td>
<td>-</td>
<td>-5.52</td>
<td>-</td>
</tr>
</tbody>
</table>

\(\textsuperscript{a}\) Estimated by (2,2)CASPT/cc-pVDZ//UM05-2X/6-31G(d,p) calculations based on a simplified models by replacing \textit{tert}-butyl groups with hydrogens.

\(\textsuperscript{b}\) Experimental value from ref. 7c.

The susceptibility in all cases discussed here is primarily due to the low lying triplet state of the $\pi$-dimer. The other are magnetically silent, but influence the susceptibility as discussed below. (The triplet states of the $\sigma$-dimers are too high to be significant in the temperature range considered.) For the dimeric pairs with crossing cofacial stacking, three dominant tautomers were found in the ground states, therefore, a four energy level scheme is used as depicted in Scheme 4.4a, where, by taking the energy of the triplet state of the $\pi$-dimer as the origin, $J_2$, $J_1$ ($\Delta E_{st}$), and $J_3$ are the relative energies of $\sigma$-dimer 12, the singlet state $\pi$-dimer 9, and of the degenerate $\sigma$-dimer 8, respectively.

The corresponding $\chi T$ is calculated by equation (4.4),
\[
\chi_T = \frac{2Ng^2\beta^2}{k[3 + \exp(-J_1/kT) + \exp(-J_2/kT) + 2\exp(-J_3/kT)]}
\] (4.4)

\(k\) is the Boltzmann constant, \(N\) is Avogadro’s constant, \(g\) is the gyromagnetic factor, \(\beta\) is the electronic Bohr magneton.

For the dimeric pairs with anti-parallel cofacial arrangement, a three energy level model (Scheme 4.4b) was used, where, by taking the energy of the \textit{anti-\pi} dimer 17 in its triplet state as energy reference, \(J_1 (\Delta E_{\text{st}})\) and \(J_2\) correspond to the energy level of \textit{anti-\pi} dimer 17 in its singlet State and of \textit{anti-\sigma} dimer 15, respectively. Equation (4.3) was used to calculate the \(\chi_T\)

\[
\chi_T = \frac{2Ng^2\beta^2}{k[3 + \exp(-J_1/kT) + 2\exp(-J_2/kT)]}
\] (4.5)

where the parameters have similar meanings to those in equation (4.4).

**Scheme 4.4.** The schematic energetic diagrams for the four-level (left) and three-level dimeric systems (right). Numbers in parenthesis indicate degeneracies. T, Triplet state; S, Singlet state. Triplets states arising from the \(\sigma\)-dimers are too high to affect the susceptibility in the relevant temperature range.
The estimated ground state energies for the \( \pi \)-dimer 9 and 17 and those of the related \( \sigma \)-dimers are listed in Table 4.7 together with that of the parent phenalenyl system 4 for the purpose of comparison. The respective \( \chi T \) plots versus temperature (\( T \)) are shown in Figure 4.7. The calculated paramagnetic susceptibility for 4 and crossing dimeric systems 9 are in good agreement with the ESR measurements.\(^7c\) Our calculations indicate that 17 has slightly larger \( \Delta E_{\text{st}} \) than 9, and accordingly shows a somewhat smaller magnetic susceptibility. Both susceptibilities indicate that these two molecules change shape except at very low temperatures and the fluxional nature of the inter-DAzPh \( \sigma \)-bonds are reflected in their magnetisms.

\[ \chi_{\text{para}} T \text{ vs } T \]

Figure 4.7. Calculated \( \chi_{\text{para}} T \) versus \( T \) curves based on the energy levels in Table 6 using Bleaney-Bower model and equations 2 and 3.

4.8 Conclusions

With the validated UM05-2X method, our calculations show that DAzPh can dimerize with two different cofacial stacking dipole orientations, i.e., the crossing arrangement observed
by X-ray diffraction and anti-parallel arrangement predicted by our calculations. The corresponding dimers with the two stacking orientations are very close in energy, and we predict that the anti-\(\sigma\)-1 dimers (15) might be isolated under suitable conditions.

Our calculations indicate that both cross-\(\sigma\)-1 (8) and anti-\(\sigma\)-1 (15) can easily undergo sigmatropic rearrangements with low barriers 10.21 kcal/mol and 11.14 kcal/mol, respectively, indicating fluxional inter-phenalenyl \(\sigma\)-bonds among several \(\sigma\)-bonded tautomers connected by a common \(\pi\)-dimer. For the rearrangement of the cross-\(\sigma\)-1 dimer, the cross-\(\pi\)-dimer intermediate was identified upon breaking the \(\sigma\)-bond. Two competitive exit channels were found to form the cross-\(\sigma\)-1' (8') and cross-\(\sigma\)-2 (12) that corresponds to degenerate [5,5] sigmatropic rearrangement and nondegenerate [3,3] sigmatropic rearrangement, respectively. The [5,5] mode is energetically favorable compared to the [3,3] rearrangement. For the anti-\(\sigma\)-1 dimer (15), the rearrangement is also a stepwise process, and only the degenerate [7,7] sigmatropic arrangement was found energetically favorable. Thus we observed a complete spectrum of sigmatropic rearrangement reactions in these radical dimers leading to unusual and facile tautomerization pathways.\(^3^2\)

The (2,2)CASPT2 excitation energy calculations, HOMO-LUMO gaps and natural orbital analysis indicate that the parent phenalenyl \(\pi\)-dimer (4), the cross-\(\pi\)-dimer (9), and the anti-\(\pi\)-dimer (17) show decreasing order of SOMO-SOMO splitting, in line with the observed UV-vis absorbance. We attribute this to the depletion of electron density at the nitrogen sites in the SOMO of D AzPh (7) radicals. In addition, the calculations suggest thermally accessible paramagnetic triplet state for the predicted dimeric systems with anti-parallel stacking.
Considering its great likelihood to be isolated, we suggest that more experimental work would be worthwhile.

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References


Note that the binding energy of the phenalenyl p-dimer has also been reported in ref. 19c, where CASSCF(2,2)/MRMP2, a similar theory level as PP(1)-MP2, was used for the calculations. However, the BSSE corrections was not included, which might overestimate the binding energy for configuration calculations. Herein, we take the PP(1)-MP2 calculated energy (ref. 16a) for comparison.


29 Phenalenyl as a one electron acceptor can form groups 2 and 12 slip sandwich complexes with various hapticities, as indicated by S. Craciun and K.J. Donald, *Inorg. Chem.*, **2009**, *48*, 5810. The lower symmetry SOMO of 8 may enhance the stability of some of these complexes.

30 Defined as the $E_{\text{bind}} = E(\text{dimer}) - 2 \times E(\text{monomer})$.


Phenalenyl is a remarkably stable odd alternant neutral hydrocarbon radical that has attracted considerable interest recently as a key motif in new materials with promising magnetic, optical and electronic properties. Its application as the core component of a new class of neutral organic conductors is well established and motivates innovative synthetic work. Phenalenyl, the precursor of the phenalenyl radical, has been proposed to undergo six-fold valence tautomerism as described in Scheme 5.1, in which the benzylic-allylic hydrogen transfer reactions are hypothesized to occur through a unimolecular process. NMR spectroscopy studies showed that the reactions designed to obtain 1-alkyl-phenalenenes, yielded a mixture of five kinds of isomers indicating that hydrogen transfer occurs in solution. However, the mechanism of this reaction has not been discussed in the literature.

Scheme 5.1. The schematic six-fold valence tautomerism hypothesized to occur in a unimolecular process.

The presented computational investigations revealed that the hydrogen transfer of

phenalene most likely proceeds through a multistep bimolecular process instead of a unimolecular process. The unusual stabilization of the biradicaloid intermediate is due to the excellent overlap of the two singly occupied molecular orbitals (SOMOs). The orientation specific stabilizing effect of the SOMO-SOMO bonding interaction has been subject of much recent research as a new intermolecular bonding type\(^9\) that plays critical roles in organic conductors\(^4\). This stabilizing effect of two \(\pi-\pi\) bonded radicals has been recently shown to play a key role in providing evidence for the stepwise mechanism of the Cope rearrangement of certain phenalenyl dimers.\(^{10}\) The same stabilizing effect makes the hydrogen transfer in the saturated phenalene preferable via a bimolecular hydrogen transfer. As we showed here, the tendency of the stepwise pericyclic mechanism has a relative low barrier due to the SOMO-SOMO \(\pi-\pi\) interactions of phenalenyl radicals. The SOMO-SOMO stabilizing effect therefore might have broader mechanistic implications than recognized before.

First, we examined the possible unimolecular process. The migration of H\(^a\) from C1 to C2 or C6, as shown in Scheme 5.1, corresponds to suprafacial [1,3] sigmatropic rearrangement, which is thermally prohibited according to Woodward-Hoffmann rules. A transition structure corresponding to [1,3] hydrogen transfer can not be located by our UB3LYP calculations with Gaussian 03 program\(^{11}\). Only a dissociative path was found when the allylic C–H bond was breaking. In addition, we investigated the two-step [1,3] hydrogen shift mechanisms as illustrated in Scheme 5.2. The phenalene reactant first undergoes suprafacial [1,2] hydrogen shift from C1 to C7 yielding a biradical intermediate that in turn undergoes another [1,2] hydrogen shift from C7 to C2 as depicted in Scheme 5.2. The UB3LYP calculated barrier
from the reactant to the intermediate is very high at 52.82 kcal/mol in terms of enthalpy, which strongly indicates that the unimolecular rearrangement is not viable. It is noted that the intermediate 2 has been detected during the epimerization of naphthocyclopropane (R. M. Pagni, M. N. Burnett, H. M. Hassaneen, Tetrahedron, 1982, 38, 843-851).

**Scheme 5.2.** The [1,3] hydrogen shift by the proposed two-step mechanism corresponding to a biradical intermediate. The optimized C-H distances are listed in angstroms. The enthalpies relative to 1 are listed below the structure number.

In addition to pathways described in Scheme 5.2, another [1,3] hydrogen shift from C1 to C6 was described in Scheme 5.3. The corresponding barrier is 60.60 kcal/mol. The electronic energies were calculated by UB3LYP/6-311+G2dp/UB3LYP/6-31G(d,p). The thermal corrections were calculated by UB3LYP/6-31G(d,p).

**Scheme 5.3.** The [1,3] hydrogen shift by the proposed two-step mechanism corresponding to a biradical intermediate. The optimized C-H distances are listed in angstroms.
We proposed a bimolecular hydrogen transfer process as described in Scheme 5.4. (Experimental information on the concentration dependence is lacking.) The allylic hydrogen, $H^a$, of a phenalene molecule 1 reacts with another phenalene molecule 1 by a stepwise ene-like reaction mechanism producing a phenalenyl radical 4 and a dihydrophenalenyl radical 5. The radical intermediates can continue the reaction by accomplishing the ene reaction (path c) and producing the dimer 7. On the other hand, the $H^a$ on radical intermediate 5 can transfer back to the phenalenyl radical 4 through a retro-ene reaction. Because of the $D_{3h}$ symmetry of the phenalenyl radical 4, the $H^a$ can randomly transfer to any of the six active $\alpha$-carbons of 4, which leads to the exchange of the allylic hydrogen ($H^a$) positions, corresponding to the six-fold isomers in Scheme 5.1. It is noted that only the hydrogen transfer from C1 to C2 is illustrated for the reto-ene reaction (path b) in Scheme 5.4.

**Scheme 5.4.** The proposed bimolecular hydrogen transfer of phenalenes.
UB3LYP calculations\textsuperscript{12} were used to confirm the viability of the proposed Scheme 5.4 (UM05-2X calculations were also done obtaining similar barriers). The energy levels calculated in the gas phase at 298 K are shown in Figure 5.1, in which the sum of the energies of two isolated phenalenones is taken as the origin. A transition structure 6 (Figure 5.2) was identified that connects the reactants and the intermediates of radicals 4 and 5. The barrier of 27.56 kcal/mol is considerably lower than the barrier of the unimolecular process. The calculated activation entropy of \(-40.6\) eu is close to that of parent ene reaction and other intermolecular ene reactions.\textsuperscript{13} The activation entropy increases the barrier in terms of free energy. However it is still considerably lower than the barrier of intramolecular process. The bridged CH distances in the transition structure are very similar to those in the parent ene reaction between propene and ethylene.\textsuperscript{14} However, the barrier is much lower than that of the parent ene-reaction (35 kcal/mol) and that of the related ene-reactions (37.0 kcal/mol for the ene reactions between ethylene and \textit{trans}-2-butene).\textsuperscript{13} Most noticeably, the transition structure 6 proceeds to the intermediates of 4 and 5, in contrast to the concerted mechanism of the parent ene reaction.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure51.png}
\caption{The energies of the bimolecular hydrogen transfer reaction and the competitive dimerization reactions.}
\end{figure}
Furthermore, in the TS, as shown in Figure 5.2, the atoms C3, C2, C13, H10, C25, and C24 form a six member ring. The NMR calculations showed that the nucleus independent chemical shift (NICS) value\textsuperscript{15} at the centre of the ring is -10.80 ppm indicating strong aromatic character (in comparison with -8.00 ppm at the centre of benzene). Accordingly, the transition state is stabilized by aromaticity providing reduced activation energy. We also noticed the extremely short interring C-C contact in 6 (at 3.005 Å compared to the van der Waals contact of 3.4 Å) which is indicative of π–π bonding based on the overlap of the two SOMOs involved,\textsuperscript{9} which we take as another indication of the unique barrier-lowering effect of these electronic π–π bonding interactions.

![Figure 5.2](image.png)

**Figure. 5.2.** The UB3LYP calculated transition structure 6 for the bimolecular hydrogen transfer reaction. The selected bond distances are in angstroms.

Figure 5.3 shows the highest occupied molecular orbital (HOMO) of TS 6. The HOMO of 6 can be traced back to the bonding combination of, and the good overlap between the SOMOs of 4 and 5 reflecting the electron delocalization aspect in 6 accounting for the low barrier. The
hydrogen transfer in this case can be categorized as a 3 electron/3 centre (3e/3c) hydrogen atom transfer (HAT).\textsuperscript{16}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{somo.png}
\caption{The SOMOs of the radical intermediates and the HOMO of the TS.}
\end{figure}

From the radical intermediates 4 and 5, the reaction pathway bifurcates. The radical intermediates can undergo retro-ene reactions with a barrier of 13.14 kcal/mol as shown in Figure 5.1. Owing to the $D_{3h}$ symmetry of the phenalenyl radical, the atom $H^a$ on 5 can randomly transfer to any of the six equivalent $\alpha$-positions of the phenalenyl radical 4. Consequently, the hydrogen transfer occurs in phenalene through a bimolecular process.

The competing reactions are the dimerization of the radical intermediates 4 and 5. There are three possible dimerization paths. The hetero-dimer 7 formed by a radical 4 and 5 corresponds to the product of a complete ene reaction compose of reaction path $a$ and $c$ in Scheme 5.4. The enthalpic barrier corresponding to this dimerization is 7.20 kcal/mol. The homo-dimerization of two radicals 4 or two radicals 5 produces the dimers 9 or 8, respectively (The transition structures are shown in Figure 5.4). As indicated by the data shown in Figure 5.1, the energies of the hetero-dimer 7 are significantly higher than the energy of the sum of two phenalene
molecules. Therefore, the hetero-dimerization reaction is less favoured compared to the hydrogen transfer interaction corresponding to path $b$ in Scheme 5.4. However, the sum of energies of the homo-dimer 8 and 9 is very close to four times of the energy of phenalene (indicated by $\frac{1}{2}(8+9)$ in Figure 5.1.). By taking the average, the homo-dimer product lies 1.22 kcal/mol above the energy of a phenalene molecule. Accordingly, the homo-dimerization might be competitive with the retro-ene reactions.

![Figure 5.4](image.png)

**Figure 5.4.** The structures of the transition state connecting to: (a) the intermediacies 4, 5 and dimer 7; (b) the intermediates 5 and 9; (c) the intermediacies 4 and 9.

In addition to the radical intermediates 4 and 5, further radical intermediates 10-20 (Figure 5.5) might be generated by the ene reaction mechanism. However, as listed in Fig. 4, the energies of these radical intermediates are all significantly higher than that of the 5. (The reason for these differences can be traced back to $\pi$-electron delocalization.) Accordingly, the respective barriers from the reactant to these radical intermediates are much higher than the barrier corresponding to
the radical intermediate 9. Therefore, the hydrogen transfers via the intermediates 10-20 are unlikely and can be ruled out.

![Figure 5.5](image)

**Figure 5.5.** The possible radical intermediates produced by the ene reactions of phenalenes. The energies (in kcal/mol) relative to 5 are shown below the number of the structures.

In conclusion, the hydrogen transfer of phenalenes occurs through a bimolecular process by stepwise ene mechanism instead of the six-fold valence tautomerism through a unimolecular process. The relatively low activation barrier and the stability of the radical intermediates arise from the high $\pi$-conjugation and the electron delocalization through a six-member ring. Together with the stepwise Cope rearrangement of the phenalenyl $\sigma$-dimer in our previous studies, the bimolecular hydrogen transfer in the hydrogenated phenalenyl show the importance of the SOMO-SOMO stabilization in the reaction mechanisms involving derivatives of large stable neutral radicals, such as phenalenyl.
References


The 1-alkyl-phenalenenes were not observed because of its relatively higher energies than the other five tautomers.


All the geometries were optimized by UB3LYP/6-31G(d,p). Single point energies were calculated by UB3LYP/6-311+G(2d,p) based on the optimized geometries. The thermal corrections are calculated at the UB3LYP/6-31G(d,p) level.


**CHAPTER 6**

**ELECTRONIC STRUCTURE OF HELICENES, C₂S HELICENES, AND THIAHETEROHELICENES**

### 6.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) have received much interest as organic semiconducting materials.¹ One of the well-studied series of these compounds is oligoacenes, which are linearly fused benzene rings as represented in 1 and 2.

![Pentacene (1)](image1)

![Hexacene (2)](image2)

The largest member of acenes synthesized so far is hexacene (2), the application of which is limited by its environmental instability. Higher member acenes, such as heptacene, are quite reactive.²³ Mondal et al. recently showed that heptacene with fair stability can be fabricated in a polymer matrix.⁴ Among the oligoacenes, pentacene (1) is considered as the most promising molecular conductor and semiconductor due to its outstanding charge carrier mobility⁵ with applications as organic field-effect transistors (OFETs). In order to understand the electronic properties, the electronic structure of oligoacene and hypothetical polyacene has attracted attention from many researchers. Tight binding calculation based on Hückel model predicted zero gap for polyacene.⁶ However, Peierls distortion splits the degeneracy at the Fermi level⁷ resulting in a small but nonzero band gap.

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Another series of annulated oligoarenes is phenacenes, starting with phenanthrene (3), chrysene (4), and picene (5).

Along with polyacenes, they can serve as models for the edge structure of graphene and carbon nanotubes. \(^8\) Experimental \(^9\) and theoretical \(^10\) studies reveal that phenacenes are more stable than their isomeric acenes. Larger band gaps have been predicted for polyphenanthrenes than for polyacenes at various theoretical levels. \(^11\) Topological effects were investigated to clarify the big band gap difference between the two systems. \(^12\)

Helicenes represent the third series of PAHs isomeric to acenes and phenacenes. Helicenes, such as pentahelicene (6), hexahelicene (7) and [11]helicene (8) adopt a well-known helical structure to accommodate the overcrowdedness of superposing rings.
The helical pitch can be approximately defined as the distance of superposing carbon atoms across the overlapping rings as sketched in 7. The first helicene model was proposed by Newman. Since then, helicenes with larger number of rings up to 14 have been synthesized. Helicenes have characteristic chiral properties arising from the helical structure. However, little attention has been paid to their electronic structures, including the band gap (or HOMO-LUMO gap), of this system probably due to the nonplanarity of the helicene chain, which was suspected to be disadvantageous for π-electron conjugation. Semiempirical Hückel and INDO calculations suggested negligible transannular interaction between the overlapping rings across the helical pitch. More recent DFT calculations indicated only a slight loss of aromatic character in helicenes despite of the nonplanarity as compared to the corresponding phenacenes. In this chapter, our discussion will focus on the comparison of electronic structure between the helical vs linear series as a function of size.

α-Oligothiophenes constitute another class of widely used π-conjugated systems. Their applications run a broad spectrum including light-emitting diodes, film transistors, and electroactive materials. Exploration of the potential surface of polythiophenes indicated two local minima corresponding to the planar anti conformation and the helical syn conformation as shown by 9 and 10.

α-thiophene with anti conformation (9)  α-thiophene with helical syn conformation (10)
The isomeric $\beta$-oligothiophenes attracted less attention possibly because of the lower degree of delocalization\textsuperscript{24} due to the steric repulsion between neighboring rings. Correspondingly, two series of fused oligothiophenes exist. The straight quasi-linear oligothienoacenes, such as heptathienoacene (11), arise from the annulation of $\alpha$-oligothiophenes. The hypothetical polymer is represented with the formula of $(C_2S)_n$\textsuperscript{25}.

![Heptathienoacene (11)](image)

A series of oligothienoacenes up to 8 thiophenes rings have been synthesized\textsuperscript{26}. Thienoacenes tend to be more planar and thereby more conjugated than $\alpha$-oligothiophene. In the crystal structure, oligothienoacenes favor more pronounced $\pi$-$\pi$ stacking\textsuperscript{26a} due to the lower ratio of C-H bonds. Such features are suggested to be favorable for charge carrier mobility, which is important for electronic and optoelectronic applications\textsuperscript{27}.

Another $(C_2S)_n$ isomer is $C_2S$ helicene (12) derived from the annulation of $\beta$-oligothiophenes.
A series of helical \((C_2S)_n\) oligomers have been recently synthesized by Rajca and Miyasaka et al.\(^{28}\) The electronic structure of linear oligothienoancene (11) has been explored at the semiempirical PM5 level,\(^{25}\) and to the best of our knowledge, such investigations on helically annealed \(\beta\)-thiophenes have not been reported. Herein, we explore the factors affecting the band gap (or the HOMO-LUMO gaps) for the two series of fused thiophene oligomers and related hypothetical polymers based on DFT calculations and qualitative orbital analysis.

Another related group of helical molecules are conjugated thiaheterohelicenes, in which thiophene and benzene rings are ortho-fused in an alternating fashion as displayed by hexathiahetero[11]helicene (13).\(^{29}\) A significant advantage of such helical conjugated molecules is their established synthesis and good yield.\(^{30,31}\) The presence of sulfur atoms in the helicene backbone offers opportunities to modify their electronic, linear and nonlinear optical properties.\(^{32}\)
In this article, structural and electronic properties were investigated at the DFT level covering helicenes, C$_2$S helicenes and thiaheterohelicenes. Further calculations were also performed on phenacenes and thienoacenes due to their structural similarity to isomeric helicenes and C$_2$S helicenes, respectively. The band gaps were calculated from oligomer extrapolations and with periodic boundary condition (PBC) calculations if possible. The calculated results were compared with structural and optical experiments wherever data are available helping to control the reliability of the theory level we used.

6.2 Computational Methodology

All DFT calculations were performed with the Gaussian 03 program. The geometry optimizations were carried out with Becke’s three parameter (B3) hybrid exchange functionals combined with Lee-Yang-Parr (LYP) correlation functionals (B3LYP). For a series of shorter oligophenacenes and oligothienoacenes, the unconstrained geometry optimization gave rise to $C_{2v}$ and $C_{2h}$ symmetry for oligomers with odd and even number of rings respectively, in agreement with the corresponding X-ray structures. Therefore, geometry optimization was constrained with $C_{2v}$ or $C_{2h}$ symmetry for larger oligomers. The geometry optimization on helicenes, C2S helicenes and thiaheterohelicenes was constrained to a $C_2$ geometry based on
similar validation for phenacenes and thienoacenes. The geometry was also optimized with PBC calculations for the phenacene and thienoacene polymer at the same level as for the corresponding oligomers.

For helical systems, a screw operation is characterized by a rotation $\theta$ and a translation $h$ per repeat unit along the screw axis as shown in Figure 6.1. A helical system remains invariant if one repeats the screw operation $l$ times ($l$ is an integer), which corresponds to a rotation of $2\pi ql$ followed by a translation of $a = lh$, where $\theta = 2\pi q$ is defined as the rotation angle. If $q$ is a rational number ($m/n$), then translational symmetry can be defined along the screw axis (usually denoted as $mn$), and periodic boundary conditions can also be defined. When $q$ is an irrational number, translational symmetry does not exist. For infinite phenacene and thienoacene, $\theta = \pi$, $q = 1/2$, and the translational vector along the screw axis has the length of $a = 2h$. For helicenes, PBC calculations were performed based upon the fact that, as discussed in the next section, helicene has a close to $6_1$ symmetry, which means $l = 6$, $q = 1/6$, and $a = 6h$. The symmetries of $C_2S$ helicenes and thiaheterohelicenes are close to $26_3$ and $7_2$, respectively. PBC calculations would be possible but costly in these cases, because of the large number of atoms in each translational unit cell.
Band gaps were calculated through two supplementary approaches, HOMO-LUMO gap extrapolations for oligomers and PBC calculations for polymers. All geometries were fully optimized except for the imposed translational symmetry in the PBC calculations. We used the B3LYP hybrid density functional with the 6-31G* basis set. The applicability of B3LYP/6-31G* to geometry optimization and to band gap calculations has been discussed, and it was suggested to predict values in good agreement with experiment for various π-conjugated systems.

Semi-empirical periodic calculations were carried out for all systems studied in this chapter using the Longuet-Higgins and Salem (LHS) method in order to develop a qualitative orbital analysis. The LHS method is a semi-empirical model with one π orbital per each C and S atom, in which only π–electrons are considered within the tight-binding (Hückel) approximation using bond distance dependent transfer (resonance) integrals. The calculations in this article are based on the LHS model parameterized by Kürti and Surjan. All geometries were relaxed in the
LHS calculations. The translational unit cells of phenacene and thienoacene contain two unit cells defined by the screw axis of symmetry. This leads to a two-fold back-folded band structure for the PBC calculation at the DFT level compared to that at the LHS level, in which the unit cells are related by the screw axis of symmetry. For helicenes, assuming a $6_1$ symmetry, the unit cell is six-times larger at the DFT level compared to that at the LHS level because the translational unit cell contains six $C_4H_2$ units based on the screw axis of symmetry. Correspondingly, the reciprocal lattice vector for PBC calculation at DFT level is six times smaller than that at the LHS level, but due to the backfolding, it has six times as many energy bands. The notation in the band structures reflects this difference: in the LHS bands, the k space varies from 0 to $\pi/h$, while in the translational PBC based DFT calculations it varies from 0 to $\pi/a$ ($a=6h$). The DFT bands are presented in the reduced Brillouin zone (BZ) where the translational unit cell has the length of $a=2h$ or $6h$. For comparison, we will present the band structure of the LHS model both in the reduced BZ and in some cases also in the extended (0 to $\pi/h$) BZ. In the band structure diagrams, only bands originating from the $\pi$ electrons are given. On some band diagrams, band crossings occur due to band back-folding. For one dimensional periodic systems with a translational vector of $h$, when the unit cell is enlarged n-fold, the corresponding translational vector is also increased to $a=nh$. Then, the BZ is reduced to the range of $[-\pi/a, \pi/a] = [-\pi/nh, \pi/nh]$, which is called reduced BZ. The original zone of $[\pi/h, \pi/h]$ is called the extended zone. Each band in the reduced BZ can be obtained by “backfolding” n-times the bands in the extended BZ. Some of these backfolded bands may cross each other in the reduced BZ, if they happen to have the same energy in the extended BZ. However, for the bands,
which avoid a crossing in the extended BZ, the avoided crossing is also reflected in the folded bands in the reduced BZ.

6.3 Results and discussion

In the next sections, the discussion was divided into three parts, phenacene and helicene; thienoacene and C$_2$S helicene; and thiaheterohelicene aiding the comparison between the corresponding linear and helical molecules. In each section we discuss the geometry, the electronic structure and their relationships.

6.3.1 Geometry optimization of phenacenes and helicenes

The HOMO-LUMO gap or band gap is dependent on the geometry, especially on bond length alternation (BLA). It is commonly accepted that Hartree-Fock (HF) and local spin density approximation (LSDA) overestimates and underestimates BLA, respectively, while DFT with hybrid functionals such as B3LYP predicts more realistic intermediate BLA values.$^{42}$ Table 6.1 lists the characteristic bond distances of chrysene (4) and [11]helicene (8).

![Figure 6.2](image-url).

**Figure 6.2.** Bond distance labels used in Table 6.1, (a) Chrysene (4); (b) [11]helicene (8).
Table 6.1. Bond distances for chrysene (4) and [11]helicene (8) from crystal structure and geometry optimization using B3LYP/6-31G*. The bond distances in the middle rings are labeled in Figure 6.2. For [11] helicene, the geometry was optimized with a $C_2$ symmetry constraint.

<table>
<thead>
<tr>
<th></th>
<th>Unit (Å)</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chrysene (4)</td>
<td>Optimization</td>
<td>1.364</td>
<td>1.427</td>
<td>1.428</td>
<td>1.453</td>
<td>1.418</td>
<td>1.431</td>
</tr>
<tr>
<td></td>
<td>X-ray$^{43}$</td>
<td>1.331</td>
<td>1.417</td>
<td>1.417</td>
<td>1.453</td>
<td>1.402</td>
<td>1.437</td>
</tr>
<tr>
<td></td>
<td>X-ray$^{44}$</td>
<td>1.348</td>
<td>1.420</td>
<td>1.427</td>
<td>1.451</td>
<td>1.413</td>
<td>1.425</td>
</tr>
</tbody>
</table>

These two molecules are the largest ones for the phenacene and helicene series, available in the Cambridge Structural Database (CSD). (The X-ray structure for picene (5) appears erroneous,$^{45}$ since the a-type peripheral bond is not the shortest in the middle ring in ref. 45.). Only the bond distances in the middle rings are listed, because they are least affected by end effects. For helicenes, the shortest carbon-carbon (CC) contacts across the helical pitch are around the van der Waals distance of carbon. For example, the shortest CC distance is 3.14 Å, a mean value from 36 hits with a hexahelicene scaffold in CSD.$^{46}$ The shortest CC distance in [11] helicene is around 3.4~3.5 Å as shown in Table 6.2. It is well known that DFT at the level used here is usually unable to describe dispersion forces accurately. However, it still predicts accurately the bond distances as listed in Table 6.1. The optimized geometries fit well with the experimental values. Coincidently, the optimized helical pitch values for [11]helicene are in fair agreement with the X-ray structural data as presented in Table 6.2.
The inner and outer values correspond to the distances between the superposed carbon atom pairs on the inside and the periphery of the helix, respectively.

<table>
<thead>
<tr>
<th>Helical Pitch (Å)</th>
<th>Inner</th>
<th>Outer</th>
<th>Average</th>
</tr>
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<tr>
<td>PBC optimization (6&lt;sub&gt;1&lt;/sub&gt; symmetry)</td>
<td></td>
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</tbody>
</table>

<sup>a</sup>Ref. 44

We conclude that B3LYP/6-31G* is sufficiently reliable for geometry optimization for these systems. To examine the constraint of PBC on the optimized geometry, relatively longer oligomers were optimized, and the bond distances on the middle ring were compared with the corresponding distances optimized using PBC. [25]phenacene and [30]helicene were chosen for this purpose. The two approaches gave nearly the same bond distances for both phenacene and helicene as presented in Table 6.3. While these systems display aspects of delocalized $\pi$-electron conjugation, oligomers of the size of 25 and 30 rings are sufficiently long to display the key characteristics of the infinite systems. This finding is useful, especially in the cases where periodic calculations are not practical, as discussed for the sulfur containing helicenes later on.
Table 6.3. Optimized bond distances (in Å) for infinite phenacene and helicene using PBC, and for the central rings of [25]phenacene and [30]helicene at B3LYP/6-31G*. The bond distances are labeled in Figure 6.2.

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenacene (PBC-DFT)</td>
<td>1.367</td>
<td>1.425</td>
<td>1.419</td>
<td>1.449</td>
</tr>
<tr>
<td>Helicene (PBC-DFT)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.363</td>
<td>1.426</td>
<td>1.426</td>
<td>1.456</td>
</tr>
</tbody>
</table>

<sup>a</sup>Assuming a $6_{11}$ helix.

For helicenes, our calculations for a series of oligomers indicated that the helicene chain approached an approximate $6_{11}$ symmetry as the number of rings increased. Therefore, the unit cell can be limited to a reasonable size ($6\times C_4H_2 = C_{24}H_{12}$) making the PBC-DFT computation practical. The optimized helical pitch values are listed in Table 6.2. The rings tilt inward for shorter oligomers like [11]helicene, and tend to become more parallel for longer oligomers as shown for [30]helicene. Despite the tilt, the average pitch values for both [11] and [30]helicene are similar to the pitch from the PBC calculation, and are close to the experimental values for [11]helicene. Some double bond localization can be observed in both systems at the peripheral a-type bonds (as labeled in Figure 6.2). The longest bonds occur at the “inner” d-type bonds. The corresponding bond distances are very close for infinite phenacene and infinite helicene as shown in Table 6.3.
6.3.2 Band gap of phenacenes and helicenes

Two complementary approaches were employed to calculate the band gap, $E_g$. The first is based on the HOMO-LUMO energy difference of oligomers, and the second comes from PBC calculations of the infinite polymer model. The HOMO-LUMO gaps were calculated with B3LYP/6-31G* for a series of oligomers containing up to 26 and 30 rings for phenacenes and helicenes, respectively. The band gaps for the polymers were obtained by extrapolating to infinite size from the oligomer data.\textsuperscript{47, 48, 49} Figure 6.3 shows the quadratically fitted HOMO-LUMO gap values as a function of the reciprocal of the number of $\pi$ electrons for phenacene and helicene systems.

![Graph showing band gap as a function of reciprocal of number of $\pi$ electrons](image)

**Figure 6.3.** B3LYP/6-31G* calculated HOMO-LUMO gaps for oligomers of phenacenes (squares) and helicenes (diamonds) as a function of $1/N_\pi$. $N_\pi$ is the number of $\pi$ electrons.
Quadratic fits and the corresponding statistics are also shown. Oligomers with up to 26 and 30 rings were used for phenacenes and helicenes, respectively.

Table 6.4 lists the band gaps obtained by the two approaches. The extrapolated band gap for helicenes is 2.90 eV, while that for phenacenes is 3.60 eV. PBC calculation indicated a direct band gap of 3.59 eV for phenacene, and an indirect band gap of 2.90 eV for helicene. These two pairs of values obtained by the two different routes for each system are sufficiently close to accept them as essentially converged values. The optical band gap obtained from experiments is 2.5 eV for helicene (extrapolated by $\lambda_{\text{max}}$ vs $1/n$, $n=6-9$), which is smaller than the calculated value, 2.9 eV. One of the possible reasons is that for the HOMO-LUMO method, the optical absorption is approximated by the one electron vertical excitation from the HOMO of the ground state to the virtual orbital represented by LUMO. Therefore, HOMO-LUMO gap is larger than the experimental optical absorption, which includes the exciton transition energy. The argument is supported by the fact that the calculated absorption spectra by TD-DFT method are in good agreement with experiment for [n]helicene ($n = 4-7$, and 12). As far as the band gap is concerned, the assumption of the perfect $6_1$ helix structure for the infinite helicene also appears as a reasonable approximation. Due to the overcrowdedness of helicene molecules across the helical pitch, the helicene chain is nonplanar, therefore the conjugation is partially reduced. Therefore, the HOMO-LUMO gaps of helicenes might be expected to be larger than those of the corresponding phenacenes. However, for the systems larger than six rings, helicenes have smaller HOMO-LUMO gaps than phenacenes as shown in Figure 6.3.
Table 6.4. Calculated band gaps for phenacene and helicene (in eV). HOMO-LUMO gaps and PBC-DFT gaps were calculated at the B3LYP/6-31G* level and compared with the PBC calculations at the LHS level.

<table>
<thead>
<tr>
<th></th>
<th>HOMO-LUMO extrapolation, DFT&lt;sup&gt;a&lt;/sup&gt;</th>
<th>PBC-DFT</th>
<th>PBC-LHS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenacene</td>
<td>3.60</td>
<td>3.59</td>
<td>2.55</td>
</tr>
<tr>
<td>Helicene</td>
<td>2.90</td>
<td>2.90</td>
<td>2.70</td>
</tr>
</tbody>
</table>

<sup>a</sup>Extrapolation range: phenacene, 3-26 rings; helicene, 3-30 rings.

The 2-fold back-folded band structure calculated with the LHS model is shown in Figure 6.4a. The DFT calculated band structure for phenacene is shown in Figure 6.4b. Note that the band crossing for phenacene is symmetry forbidden in Figure 6.4. The avoided crossing can be clearly seen from the band plot in the extended BZ. The similarity between the two band structures suggests that the semiempirical LHS model is capable to predict qualitatively the electronic properties of this extended system. Both of them indicate a direct band gap at $k=0$, and qualitatively, the overall bandwidth values are similar.
In order to analyze the geometrical and electronic structures, a qualitative orbital analysis has been performed. The highest occupied crystal orbitals (HOCO) and lowest unoccupied crystal orbitals (LUCO) at k=0 were constructed from atomic $\pi$ orbitals, which are shown in Figure 6.5a and 6.5b. The nodal pattern of the HOCO indicates a dominant contribution from the isolated ethylene HOMO orbital located on the a-type bonds as labeled in Figure 6.2, while the nodal pattern of LUCO is characteristic of a quinonoid form of cis-PA composed of the c-type and d-type bonds.\textsuperscript{25} According to the \textit{fully optimized} geometry, the peripheral a-type bonds are highly
localized resulting in a lower HOCO level. The optimized central d-type bonds are stretched significantly (compared to standard C=C bonds, or a-type bonds) and the degree of bonding character is reduced on these bonds, which leads to higher LUCO level. Therefore, unsubstituted phenacenes have relatively large band gaps. We also notice from the band structures, that at k=0, the energy levels of the two highest valence bands (HOCO and HOCO-1) are very close (Actually, these two bands correspond to the unfolded HOMO band at the LHS level). Similarly, the two lowest conduction bands (LUCO and LUCO+1) are almost equal (They correspond to the unfolded LUMO band at the LHS level). The orbital diagrams of the HOCO-1 and LUCO+1 are shown in Figure 6.5c and 6.5d, respectively.

![HOCO (a) vs LUCO (b)](image1)

![HOCO-1 (c) vs LUCO+1 (d)](image2)

**Figure 6.5.** Illustration of orbital diagrams at k=0 for infinite phenacene, corresponding to Figure 6.4b.
Note that the energy level of the HOCO is sensitive to the peripheral a-type bond length, while the HOCO-1 is more sensitive to the BLA of the cis-PA. Similarly, the LUCO is sensitive the BLA of the cis-PA, while the LUCO+1 is more sensitive to the peripheral a-type bond length. For substituted phenacenes, the HOCO might correspond to the orbitals shown in either in Figure 6.5a or 6.5c, depending on how the geometry is affected by substitution. Likewise, the LUCO might correspond to the orbitals shown in either Figure 6.5b or 6.5d.

Phenacenes and helicenes have similar local connectivities.\textsuperscript{53} The two series are closely related with respect to the corresponding bond distances as discussed in the previous section, as well as with respect to other properties, such as total energies and magnetic susceptibilities.\textsuperscript{17} Intuitively, the band gap of phenacene is expected to be smaller than that of helicene considering the nonplanarity of the latter. However, the predicted band gap for helicene at B3LYP/6-31G* level is 0.7 eV smaller than that for phenacene despite the nonplanarity of helicene. Our interest in the band gap difference between the two systems lies in the fact that it might provide an opportunity to better understand the electronic structure of conjugated helicenes. The LHS method offers a good starting point to examine the topological effect on the band gap difference between the two systems. The unit cell and bond connectivities are shown in Figure 6.6. The LHS band structure should not be directly compared to the DFT calculations. However, the trend between the gap values predicted for the two systems using LHS is the opposite of that found in the DFT calculations as can be seen in Table 6.4. According to the closeness of the two LHS values, phenacene and helicene should have similar band gaps. Therefore, there are some other factors affecting the band gap difference between the two systems.
Figure 6.6. Illustration of bond connectivities in phenacenes (a) and helicenes (b) for LHS calculations. Numbering is given for two adjacent unit cells.

We notice from Figure 6.3 that the HOMO-LUMO gaps of helicenes and phenacenes coincide for the systems with 3, 4 and 5 rings, and starting from 6 rings, the gaps started to diverge from each other. The differences become larger with the increasing number of rings. We can see from the structure of helicenes that the $\pi-\pi$ orbital overlap across the helical pitch starts from hexahelicene, which corresponds to one helical turn. With the assumption of $6_1$ symmetry as discussed above, the crystal orbitals overlap out of phase across the helical pitch at $k=0$ as shown in Figure 6.7, because the superposed $\pi$ orbitals between neighboring unit cells are in phase due to translational symmetry, no matter how the orbitals look like in each translational unit cell (one full helical turn). Correspondingly, the crystal orbitals overlap in phase at $k=\pi/6h$ (or $k=\pi/a$, $a=6h$), since the superposed $\pi$ orbitals between neighboring unit cells are out of phase. DFT calculations indicate that the HOCO is located very near to $k=0$, leading to an out of phase $\pi-\pi$ overlap, and accordingly, the energy level is raised due to the orbital interaction across the pitch.
The LUCO is located very close to $k = \pi/6h$, leading to an in phase $\pi-\pi$ overlap, and therefore the energy level is lowered.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{helical_axis}
\caption{Schematic orbital overlap diagram across helical pitch at $k=0$ and $\pi/6h$ ($a=6h$, assuming a $6_1$ symmetry).}
\end{figure}

The LHS band structure is shown in Figure 6.8, which indicates that the HOCO and LUCO are both located around $k=\pi/2h$. Figure 6.9a shows the 6-fold back-folded band structure at the LHS level. Figure 6.9b shows the energy band structure from the PBC-DFT calculation with $6_1$ symmetry. Note that the band crossings are a result of the backfolding because the levels that cross correspond to different $k$-value in the extended BZ as shown in Figure 6.8. The two band structures are similar, which means that most of the band features are predicted rather well with the LHS model excluding the $\pi$ orbital overlap effect across the pitch. We separated the factors affecting the energy level of the PBC-DFT calculated bands into two parts. One arises from the conjugation along the helicene chain, which can be approximately evaluated at the LHS level according to the similarity between the back-folded LHS bands and DFT bands.
The other part comes from the $\pi-\pi$ orbital overlap across the helical pitch, which is automatically included in the PBC calculation at the DFT level. We notice that at the LHS level, the valence and the conduction bands after back-folding are very flat meaning that the bands would be approximately independent of $k$ for the valance and the conduction bands. However, the overlap across the helical pitch is highly dependent on $k$ as discussed in connection with Figure 6.7. Compared to the LHS bands, the energy level of the conduction band moves up and is lowered at around $k=0$ and $k=\pi/6h$, respectively, as indicated by the arrows in Figure 6.9a. Similarly, the energy level of the valance band moves up and is lowered at around $k=0$ and $k=\pi/6h$, respectively. Therefore, the HOCO moves toward $k=0$, and the LUCO moves toward $k=\pi/6h$ compared to the LHS bands, as shown in Figure 6.9b. Consequently, the band gap of helicene is significantly reduced by the $\pi$ orbital overlap across the helical pitch.

\textbf{Figure 6.8.} $\pi-$band structure of helicene calculated with the LHS model. Two occupied and two empty bands are shown.
Figure 6.9. Part of the calculated band structures of helicene. (a) After back-folding of the LHS bands; (b) PBC with 6\_I symmetry at the B3LYP/6-31G* level. Five occupied and five empty bands are shown.
6.3.3 Geometry of thienoacenes and C<sub>2</sub>S helicenes

First, we compare the experimental and fully optimized geometries of [5]thienoacenes<sup>26a</sup> and C<sub>2</sub>S [11]helicene,<sup>28b</sup> which are the largest oligomers available in CSD for these two systems. The bond distances in the middle rings are used for comparison, as illustrated in Figure 6.10. Table 6.5 lists selected bond distances from X-ray and the optimized geometry for the two molecules.

![Figure 6.10](image)

**Figure 6.10** Illustration of bond distances in (a) infinite thienoacene; (b) infinite C<sub>2</sub>S helicene. Numbering is given for two adjacent unit cells. Note the cisoid polyacetylene-like chain in (a).

**Table 6.5.** Central bond distances for [5]thienoacene and C<sub>2</sub>S [11]helicene from crystal structure and B3LYP/6-31G* geometry optimization.

<table>
<thead>
<tr>
<th></th>
<th>Unit (Å)</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
</tr>
</thead>
<tbody>
<tr>
<td>[5]thienoacene</td>
<td>Optimization, C&lt;sub&gt;2v&lt;/sub&gt;</td>
<td>1.419</td>
<td>1.395</td>
<td>1.756</td>
<td>1.756</td>
<td>1.395</td>
</tr>
<tr>
<td></td>
<td>X-ray&lt;sup&gt;26a&lt;/sup&gt;</td>
<td>1.426</td>
<td>1.399</td>
<td>1.735</td>
<td>1.735</td>
<td>1.399</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;S</td>
<td>Optimization, C&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.455</td>
<td>1.393</td>
<td>1.746</td>
<td>1.746</td>
<td>1.393</td>
</tr>
<tr>
<td>[11]helicene</td>
<td>X-ray&lt;sup&gt;28b&lt;/sup&gt;</td>
<td>1.454</td>
<td>1.381</td>
<td>1.733</td>
<td>1.728</td>
<td>1.374</td>
</tr>
</tbody>
</table>
Accordingly, the corresponding CC bond distances fit very well between experiment and the optimized geometry. The optimized geometries for [7] and [11] C$_2$S helicene are in good agreement with those calculated at the similar level by Osuna et al.$^{54}$ In thiophenes, B3LYP/6-31G* systematically overestimates the CS bond lengths, e.g. for thiophene we obtained 1.736 Å as compared to MP2 calculations (1.718 Å) and the experiment (1.714 Å).$^{55}$ This is also the case for thienoacenes and C$_2$S helicenes. Based upon the good match, we assume that B3LYP/6-31G* is applicable to these types of systems. Table 6.6 lists the bond distances of thienoacene optimized with PBC at B3LYP/6-31G*. A longer oligomer, [25]thienoacene, was also optimized at the same level of theory in order to examine the PBC constraint on the geometry optimization. The bond distances in the middle ring of the oligomer were compared with the corresponding distances optimized using PBC. The two approaches give exactly the same bond distances for thienoacene as shown in Table 6.6. According to the optimized geometry of oligomers, C$_2$S helicene approaches an approximate $2\theta_3$ symmetry ($\theta=6\pi/26$) as the number of rings increases. A translational vector can be defined with each unit cell containing 26 C$_2$S units. However, the large number of atoms per such a unit cell prohibits PBC calculations at the B3LYP/6-31G* level for this system. Such a $2\theta_3$ symmetry leads to interdigitated S…S contacts across the helix pitch, and thereby good overlap between sulfurs is not expected. The a-type CC bonds is the longer of the two for both types of systems, but the difference between the a-type and b-type bonds is very small in the thienoacene case.
Table 6.6 The optimized bond distances for infinite thienoacene using PBC, and for [25]thienoacene and C₂S [30]helicene at B3LYP/6-31G* level. The bond distances correspond to the middle ring as labeled in Figure 6.10.

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thienoacene (PBC-DFT)</td>
<td>1.416</td>
<td>1.397</td>
<td>1.756</td>
</tr>
<tr>
<td>[25]thienoacene</td>
<td>1.416</td>
<td>1.397</td>
<td>1.756</td>
</tr>
<tr>
<td>C₂S helicene(PBC-DFT)(^a)</td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂S [30]helicene</td>
<td>1.457</td>
<td>1.394</td>
<td>1.742</td>
</tr>
</tbody>
</table>

\(^a\)PBC calculation is not practical for C₂S helicene because of large number of atoms in the unit cell at the \(2\bar{6}_3\) screw axis of symmetry.

6.3.4 Band gap analysis for thienoacenes and C₂S helicenes

The band gaps obtained from extrapolation and PBC calculations are listed in Table 6.7 for thienoacenes and thiohelicenes. Thienoacene has a much larger band gap than C₂S helicene for the same number of rings. Topology is an important factor to be considered in band gap engineering of organic conductors or semiconductors.\(^{56}\) There are topological reasons for such a large band gap difference between these two systems based on a qualitative orbital analysis. At first sight, it seems that the local bond connectivity is very similar, and the optimized and experimental geometry show similar bond delocalization for the two systems as shown in Table 6.5 and Table 6.6. However, a cis-PA-like backbone can be defined for polythienoacene, but not for C₂S helicene chain. The backbone of cis-PA can be considered as the starting point of the
analysis of the electronic structures for polythiophene\textsuperscript{57} and polythienoacene,\textsuperscript{25} but not for C\textsubscript{2}S helicene.

**Table 6.7.** Calculated and experimental band gaps for infinite thienoacene and C\textsubscript{2}S helicene.

<table>
<thead>
<tr>
<th>Unit (eV)</th>
<th>LHS</th>
<th>Extrapolation\textsuperscript{a}</th>
<th>PBC-DFT\textsuperscript{b}</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thienoacene</td>
<td>2.25</td>
<td>2.15</td>
<td>2.25</td>
<td>2.25</td>
</tr>
<tr>
<td>C\textsubscript{2}S helicene</td>
<td>4.12</td>
<td>4.1</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

\textsuperscript{a}HOMO-LUMO gap extrapolation calculated at the B3LYP/6-31G* level. Extrapolation range: [3]-[40]thienoacene; C\textsubscript{2}S [3]-[30]helicene.

\textsuperscript{b}PBC calculation at B3LYP/6-31G* level.

\textsuperscript{c}The band gap was extrapolated with HOMO-LUMO gaps versus the reciprocal of the number of rings. The HOMO-LUMO gap points were obtained from the UV-vis spectra of [3]-, [5]-, [7] thienoacenes.\textsuperscript{26a}

\textsuperscript{d}The band gap was extrapolated with HOMO-LUMO gaps versus the reciprocal of the number of rings. The HOMO-LUMO gap points were obtained from the UV-vis spectra of [4]-, [6]-, [8]thienoacenes.\textsuperscript{26b}

\textsuperscript{e}Experimental HOMO-LUMO gaps from reference 26b were linearly fitted as a function of the reciprocal number of \pi electrons.

Similar to the band gap discussion on hydrocarbon system, the semiempirical LHS model was used to clarify how the bond connectivity affects the band gaps of thienoacene and C\textsubscript{2}S helicene.

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The LHS calculated band structure of thienoacene is shown in Figure 6.11, which indicates a direct band gap at $k=0$. The back-folded LHS band structure and the DFT band structure are shown in Figure 6.12a and 6.12b, respectively. Both of them indicate a similar direct band gap at $k=0$ in the reduced BZ.

**Figure 6.11.** Unfolded $\pi$-band structure of thienoacene calculated by LHS. Two occupied and one empty band is shown.
Figure 6.12. The band structures of thienoacene. (a) back-folded bands at the LHS level; (b) PBC at B3LYP/6-31G* level. Four occupied and two empty bands are shown.

The following orbital analysis was based on the unfolded band structure (in the extended BZ) calculated by LHS. The backbone of thienoacene is divided into two parts: one is a set of sulfur atoms, and the leftover is reminiscent of cis-PA. Consequently, the energy bands can be approximately classified as PA bands and sulfur bands, which strongly mix with each other at certain k points. Figure 6.13a and 6.13b illustrate the orbital diagrams corresponding to the HOCO and the LU CO of cis-PA at k=0.
Figure 6.13. Orbital diagrams corresponding to the *cis*-PA bands at k=0 in thienoacene. (a) HOCO; (b) LUCO.

Note that the sulfur π-orbitals do not mix with the PA-like HOCO at k=0. However, the sulfur π-orbitals mix with the PA LUCO at k=0 with antibonding character between the π-orbitals of sulfur and the carbons directly connected to it raising the LUCO energy level. Figure 6.14 shows the orbital diagram of the HOCO and the LUCO of thienoacene. Thus, similar to ploythiophene, the band gap of thienoacene has two components, i.e. the S-C antibonding interaction in LUCO and the BLA of cis-PA backbone. The former factor enlarges the band gap. According to optimized bond lengths as shown in Table 6.6, the BLA along the PA is small for thienoacene. Therefore, the band gap is not very large with the value of 2.2 eV.

Figure 6.14. Orbital diagrams of HOCO and LUCO of thienoacene at k=0.
Figure 6.15 shows the LHS band structure corresponding to the carbon backbone. It indicates an indirect band gap with the HOCO at $k=\pi/h$ and LUCO at $k=0$. The respective orbitals are shown in Figure 6.16. The small coefficients on the inner carbons lead to a band gap larger than that of thienoacene due to the lack of efficient conjugation pathway for C$_2$S helicene.

![Graph showing band structure](image)

**Figure 6.15.** LHS calculated band structure of carbon backbone in C2S helicene.
Figure 6.16. Schematic orbital diagrams corresponding to the carbon backbone in C$_2$S helicene. (a) HOCO at $k=\pi/h$; (b) LU CO at $k=0$.

Figure 6.17. Orbital diagram of C$_2$S helicene with sulfur contribution. (a) HOCO at $k=\pi/h$; (b) LU CO at $k=0$. 
The HOCO and LUCO, after coupling with the sulfur π-orbitals, are shown in Figure 6.17. Similar to thienoacene, there is no contribution from sulfur to the HOCO due to the additional mirror planes of symmetry, but the sulfur π-orbitals couple with the LUCO. This finding is supported by the band structure of C₂S helicene as shown in Figure 6.18, where the energy level of LUCO is raised compared to the LUCO of carbon backbone (Figure 6.15) due to the S-C antibonding interaction.

![Figure 6.18](image)

**Figure 6.18.** LHS calculated π-band structure of C₂S helicene. Two of the bands are occupied.

Apart from the HOCO-LUCO mixing for C₂S helicene, which enlarges the band gap compared to thienoacene, we also notice from the optimized geometry, that the a-type bonds are much shorter for thienoacene (1.416 Å) than that for C₂S helicene (1.457 Å). This leads to an even higher HOCO level for thienoacene due to antibonding character on these bonds. Similarly,
the shorter a-type bonds distance makes the LUCO level even lower for thienoacene than that for C₂S helicene. Consequently, the band gap of thienoacene is further reduced compared to that of C₂S helicene.

Due to the helical structure of C₂S helicene, the π orbital overlap across the helical pitch might affect the band gap, which the above analysis did not yet include. As we discussed above, there is no contribution from sulfur to the HOCO. Furthermore, the in phase and out of phase π-π overlap between the superposing rings nearly cancel. Therefore, the energy level of the HOCO is not affected by the π–orbital overlap across the helical pitch. For the LUCO, there is significant contribution from sulfur. Although the distance between the mean planes of superposing rings is approximately 3.70 Å, a value close to the van de Waals distance of sulfur, an efficient overlap is not possible because of the overall approximate 26₃ structure, which creates an interdigitated network of sulfur atoms with S···S contacts calculated at 4.15-4.20Å. Therefore, the sulfur π-overlap is not significant for the energy level of the LUCO. The out of phase π–π overlap from the superposing carbon atoms might raise energy level of LUCO. However, the overlap is not efficient due to the π–π overlap cancellation between the imperfectly superposing rings. The calculated S···S distances (4.15-4.20) is smaller than the X-ray values at 4.43-4.71 for [11]C₂S helicene, but still larger than the van de Waals distance of sulfur. Since both experiment and DFT contacts are too large for effective overlap, the dispersion effect is negligible on the band structure. Accordingly, we suggest that the band gap is not significantly influenced by the orbital overlap across the helical pitch. We also learn from the orbital diagram of C₂S helicene, that nonpalanarity further enlarges the band gap.
The calculated HOMO-LUMO gap extrapolation for thienoacene is shown in Figure 6.19.

Figure 6.19. The B3LYP/6-31G* calculated and experimental HOMO-LUMO gaps for thienoacene as a function of 1/Nπ. Linear fits were used for both calculated and experimental values, and corresponding statistics are shown. The experimental HOMO-LUMO gaps was measured with the UV-vis spectra of [4]-, [6]- and [8]thienoacenes.26b (Squares: calculated HOMO-LUMO gaps; diamonds: experimental values.)

The points were linearly fitted until [40]thienoacene with an excellent correlation coefficient. The extrapolated band gap is 2.15 eV, which is close to 2.25 eV from PBC calculation. If longer oligomers were counted, the band gap from the two methods should coincide. The experimental HOMO-LUMO gaps are also shown in Figure 6.19 for [4]-, [6] and [8]thienoacenes.26b We notice that these values are systematically lower than the calculated values. The possible reason is that our calculation of the HOMO-LUMO gaps ignores important correlation effects. However, the difference between calculated and experimental values
decreased with the increase of the number of rings. The experimental HOMO-LUMO extrapolation gave band gap of 2.33 eV, which is very similar to that from the calculation.

The HOMO-LUMO extrapolation for C$_2$S helicene is shown in Figure 6.20, in which oligomers up to 30 rings were used.

![Graph showing HOMO-LUMO gaps for C$_2$S helicene as a function of $1/N\pi$. A linear fit and corresponding statistics are also shown.](image)

**Figure 6.20.** The B3LYP/6-31G* calculated HOMO-LUMO gaps for C$_2$S helicene as a function of $1/N\pi$. A linear fit, and corresponding statistics are also shown.

The extrapolated band gap is 4.10 eV, which is much larger than that of thienoacene just as predicted by the qualitative orbital analysis. The optical absorption maxima for C$_2$S [7]helicene is around 4.85 eV, which fits well with our calculation. When the absorption onset was used, the optical gap is 3.55 eV for C$_2$S [11]helicene, which is smaller than our calculation, 4.51 eV. However, the optical gap corresponding to the absorption maxima fit much better with our calculation. The justification for the difference between the calculated and experimental value is
similar to that for helicene. The possible reason is due to the near degeneracy of the HOMO level, which reduces the band gap due to vibronic coupling.\textsuperscript{54} The other possible reason is that $\lambda_{\text{onset}}$, instead of $\lambda_{\text{max}}$ was used in the experiment. The problems using $\lambda_{\text{onset}}$ is that this value might corresponds to adiabatic transition energy which is lower than vertical excitation at $\lambda_{\text{max}}$. The HOMO-LUMO gap approximation corresponds to the $\lambda_{\text{max}}$, and hence it is smaller than experimental values using $\lambda_{\text{onset}}$.

6.3.5 Geometry optimization and band gap for thiaheterohelicenes

The geometries from optimization and X-ray are listed in Table 6.8 for hexathia[11]heterohelicene. The similar calculation has been done for tetrathia[7]heterohelicene at B3LYP/6-31G**,\textsuperscript{58} and gave same bond distances as our calculation at B3LYP/6-31G*. The CC bonds opposite to sulfur atoms are the longest and peripheral bonds are the shortest just as is the case of the helicenes and C$_2$S helicene. In thiaheterohelicene, a thiophene ring is right above a benzene ring, and it tends to adopt an approximately $7_2$ symmetry with the increasing number of rings. For hexathia[11]heterohelicene, the distance between the centroids of the overlapping benzene and thiophene rings is 3.681 Å and 3.893 Å according to the optimized and x-ray geometry, respectively. Such distance for the optimized octathia[15]heterohelicene is 3.803 Å.
Table 6.8. Selected bond distances for hexathia[11]heterohelicene from crystal structure and geometry optimization at B3LYP/6-31G* level. The bonds are labeled according to Figure 6.21a.

<table>
<thead>
<tr>
<th>Unit (Å)</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
<th>f</th>
<th>g</th>
<th>h</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray</td>
<td>1.393</td>
<td>1.390</td>
<td>1.379</td>
<td>1.392</td>
<td>1.420</td>
<td>1.416</td>
<td>1.449</td>
<td>1.741</td>
</tr>
<tr>
<td>Optimization</td>
<td>1.418</td>
<td>1.400</td>
<td>1.389</td>
<td>1.400</td>
<td>1.418</td>
<td>1.429</td>
<td>1.459</td>
<td>1.759</td>
</tr>
</tbody>
</table>

Figure 6.21. (a) Bond labeling for thiaheterohelicene; (b) Schematic structure of helical poly(o-phenylene)

Thiaheterohelicene is analogous to helical poly(o-phenylene) with the removal of sulfur (Figure 6.21b). Helical poly(o-phenylene) can be used as a starting point for a qualitative orbital analysis. The HOCO and LUCO are shown in Figure 6.22. The sulfur π-orbitals are decoupled from the HOCO of poly(o-phenylene) due to symmetry, but their antibonding interactions with neighboring carbons raise the LUCO band and the band gap is enlarged similarly to C₂S
helicene. We also notice that the bonds opposite to the sulfur atoms have antibonding character in the HOCO, and bonding character in the LU CO. Compared with poly(o-phenylene), the sulfur atoms tend to reduce the CC bonds opposite to the sulfurs, and thereby reduce the bond length alternation of the PA-like chains composed of the inner carbon atoms. Therefore, the band gap is reduced.

Figure 6.22. Illustration of the HOCO and LU CO at k=\(\pi/h\) for thiaheterohelicene

Figure 6.23 shows the HOMO-LUMO gap extrapolation for thiaheterohelicene. The extrapolated band gap is 2.52 eV, which is the smallest among the helical systems covered in this study, although according to its composition, thiaheterohelicene is between the two large band gap systems, helicene and \(C_2S\) helicene. The electrochemical energy gaps have been measured with the values of 3.46 and 3.14 eV,\(^60\) respectively, for tetrathiathetero[7]helicene and hexathiathetero[10]helicene, which fit fairly well with our calculations.
Figure 6.23. B3LYP/6-31G* calculated HOMO-LUMO gaps (square) for thiaheterohelicenes as a function of $1/N_{\pi}$. Electrochemical gaps\textsuperscript{60} for tetrathiahetero[7]helicene and hexathiahetero[10]helicene are also shown (triangle).

The smaller band gap of thiaheterohelicenes compared to C\textsubscript{2}S helicene can be easily rationalized due to the lack of effective conjugation pathway of the later. For the comparison between thiaheterohelicene and helicene, the orbital analysis of helicene also starts from poly($\omega$-phenylene), as shown in Figure 6.24, where helicene is divided into two parts. Correspondingly, the energy bands are classified as poly ($\omega$-phenylene) bands and ethylene bands. Note, that the HOCO of poly ($\omega$-phenylene) couples with the LUMO of ethylene at $k=\pi/h$, thereby the HOCO is stabilized. However, for thiaheterohelicene, such stabilization is not possible. Meanwhile, for helicene, the LUCO of poly ($\omega$-phenylene) mixes with the HOMO of ethylene, therefore, the LUCO is raised. This is similar to the destabilization effect of the sulfur band on the LUCO of thiaheterohelicene. Overall, the band gap of thiaheterohelicene is reduced compared to helicene.
According to the orbital diagram of HOCO and LUCO, the in phase and out phase $\pi$-orbital overlaps cancel with each other across the superposed benzene and thiophene rings.

![Diagram](image.png)

**Figure 6.24.** Illustration of the separation of helicene into poly($\sigma$-phenylene) and ethylene. The bold bonds are the ethylene fragments.

### 6.4 Conclusions

Phenacene and isomeric helicene have similar bond connectivities, and DFT calculations indicated that corresponding bond distances are nearly identical for the polymers of the two systems. According to geometry optimization for a series of oligomers of helicene, the infinite helicene tends to adopt a close to $6_1$ symmetry. Despite of the nonplanarity, both PBC calculation and HOMO-LUMO gap extrapolation at B3LYP/6-31G* level showed that the band gap of helicene is $\sim$0.7 eV smaller than that of phenacene. With the combination of band structure and orbital analysis, we concluded that, the $\pi-\pi$ overlap across the helical pitch reduces the band gap for helicene compared to planar phenacenes.
The band gap of C\textsubscript{2}S helicene, 4.10 eV, is much larger than the isomeric thienoacene, 2.11 eV. Qualitative orbital analysis showed that the larger band gap difference is due to the lack of an effective conjugation path for C\textsubscript{2}S helicene. In addition, the optimized geometry indicated a longer CC bond opposite to sulfur for C\textsubscript{2}S helicene than that for thienoacene, which further enlarged the band gap difference between the two systems. Due to the approximately \(2\delta\) helical structure found here as the most likely structure for C\textsubscript{2}S helicene, the sulfur atoms across the pitch form an interdigitated network. The result of this structure leads to a reduced \(\pi-\pi\) overlap effect across the helical pitch.

The extrapolated band gap of 2.52 eV for thiaheterohelicene is the smallest among the helical systems covered in this study. The sulfur affects the band gap in two ways. Orbital analysis revealed that sulfur raises the energy level of LUCO and enlarges the band gap. On the other hand, it reduces the bond length alternation of the PA-like chains composed of the inner carbons, thereby further reducing the band gap. We find no evidence for a \(\pi\)-orbital overlaps significantly affecting the gaps of thiaheterohelicene.

We also pointed out difficulties in performing periodic calculations on helical systems with large translational periods but also showed how to overcome these difficulties by using extrapolations from oligomer calculations.

Acknowledgement

Financial support from the National Science Foundation (Grant No. DMR-0331710) is gratefully acknowledged.
References


Chapter 7

Low Bandgap Pyrazine Polymers: Ladder-Type Connectivity by Intramolecular S···N(sp²) Interactions and Hydrogen Bonds

Bandgap control of π-conjugated polymers is one of the important aspects of materials science.¹ For π-conjugated polymers, the molecular orbital levels of the monomers disperse into broad π-bands narrowing the energy gap between the highest occupied (HO) and the lowest unoccupied (LU) energy level.² Therefore, the bandgap is strongly affected by π-band dispersion, where larger π-band dispersion and π-electron delocalization usually go hand in hand with higher mobility and smaller bandgaps. The good overlap of the highest occupied orbitals (HOMO) and/or lowest unoccupied orbitals (LUMO) between the neighboring unit cells generally favor larger π-bandwidth (BW). Building ladder-type π-conjugated polymers can be an effective way to enhance this overlap of either or both orbitals. Following this line of argument, a number of ladder-type semiconducting polymers have been designed such as thienoacene³, polyacene⁴, acetylenic coupled ladder polymers⁵. Poly(p-phenylene) (PPP) and corresponding nitrogen heterocyclic polymers are a class of semiconducting polymers that have attracted interest.⁶ Efforts have been made to reduce the bandgaps of these polymers by planarization. One of the approaches is to build ladder polymers by bridging the repeat units through chemical bonds as shown for 1⁷, and 2⁸ in Chart 7.1. In another scheme, the polymers are planarized by

---

forming ladder-like structures through intramolecular hydrogen bonding between the neighboring unit cells as shown for \(5^9\) and \(6^{10}\) in Chart 7.1.

**Chart 7.1.** The chemical structures of: (a) \(1\) (ref. 7) and \(2\) (Ref. 8), previously synthesized ladder pyridine and pyrazine polymers; (b) \(3\) (ref. 11), non-ladder poly-(pyrazine-2,5-diyl) (PPyrz); (c) \(4\) all-carbon ladder polymer corresponding to \(1\) and \(2\). (d) \(5\) (ref. 9) and \(6\) (ref. 10), pyridine and pyrazine polymers with ladder connectivity by hydrogen bonds; (e) \(7\) is a model polymer.

\[
\begin{align*}
\text{1, } R &= \text{C}_4\text{H}_9\text{-n} \\
\text{2, } R &= \text{C}_4\text{H}_9\text{-n} \\
\text{3} \\
\text{4} \\
\text{5, } R &= \text{C}_{12}\text{H}_{25}\text{-n} \\
\text{6, } R &= \text{O-}t\text{Bu}
\end{align*}
\]
In this study, we show that these nitrogen-rich PPPs synthesized following the two strategies have large bandgaps in their undoped states. Furthermore, we propose alternative strategies to lower the bandgap by forming ladder-like polymers through intramolecular secondary interactions already known to exist. We focus on S···N(sp\(^2\)) interactions and hydrogen bonds to establish planarized low gap polymers based on pyrazine derivatives.

First, we comment on the electronic structures of the class of previously synthesized ladder polymers 1 and 2. The calculated and experimental bandgaps of ladder polymers 1 and 2 are listed in Table 7.1. The bandgap of poly-(pyrazine-2,5-diyl) (PPyz(3)) is also presented for comparison. We applied hybrid density functional theory (DFT) at the B3LYP/6-31G(d) level using periodic boundary conditions (PBC) for the polymers and molecular orbital theory for the oligomers and monomers.
Table 7.1. Calculated and experimental bandgaps (in eV) of the fused pyridine polymers and the fused pyrazine polymers. The theory level is B3LYP/6-31G(d) under PBC. The C_{12}H_{25}-n in 1 and C_{4}H_{9}-n in 2 are replaces with methyl groups in calculation to save computer time.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theory</td>
<td>3.24</td>
<td>3.13</td>
<td>3.00</td>
<td>3.16</td>
</tr>
<tr>
<td>Exp.</td>
<td>1.50 (ref. 7)</td>
<td>N/A</td>
<td>2.82 (ref. 11)</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Our PBC calculations indicate that PPyruz (3) takes planar configuration as reported before, and the predicted bandgap is in good agreement with the optical bandgap. Surprisingly, our calculated bandgap for 1 is significantly larger than the low experimental bandgaps claimed by the authors. Based on the good performance of the employed theory level for PPyruz (3) and other reported polymers, our predictions appear reliable. The likely reason for the small experimental optical gap for 1 is that it was measured in acidic media, leading to doping and thus reducing the optical bandgaps. The reason for the large calculated bandgaps of 1 and 2 is that they adopt a topology similar to polybenzanthracene (4), which has been theoretically studied to have a large bandgap. Therefore, we conclude that building ladder polymers like 1 and 2 is not effective to lower bandgaps as claimed earlier.

We now turn to the class of synthesized polymer 5, 6 and the corresponding model polymer 7 (See Chart 7.1), where the ladder-like connectivity is acted by a hydrogen bond between neighboring units. As shown in Table 7.2, our calculated bandgaps for 5 and 6 are in good agreement with the optical bandgaps. According to our PBC calculations as shown in Table 7.2, the two polymers are nonplanar, and show large bandgaps. To evaluate the effect of the
nonplanarity on the bandgaps, we calculate the bandgaps of model polymer 7. The bandgap of 7a is based on the fully optimized geometry of 7, while that of 7b is based on the geometry of 7 optimized with the dihedral angle constrained to zero degrees. Our calculations on the model polymer 7 indicate that even at the planar structure, this class of materials would still exhibit large gaps above 2.0 eV.

**Table 7.2.** The experimental and calculated bandgaps (eV), and the calculated dihedral angle ($\phi$, degrees). The theory level is B3LYP/6-31G(d,p) under PBC condition. C$_{12}$H$_{25}$-n in 5 and O-tBu in 6 are replaced with methyl groups for computation.

<table>
<thead>
<tr>
<th></th>
<th>5</th>
<th>6</th>
<th>7a$^a$</th>
<th>7b$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theory</td>
<td>$E_g$</td>
<td>3.04</td>
<td>2.55</td>
<td>2.30</td>
</tr>
<tr>
<td></td>
<td>$\phi$</td>
<td>26.37</td>
<td>13.78</td>
<td>24.54</td>
</tr>
<tr>
<td>Exp.</td>
<td>$E_g$</td>
<td>2.92(ref. 9)</td>
<td>2.78(ref. 10)</td>
<td>N/A</td>
</tr>
</tbody>
</table>

$^a$The bandgap calculated based on the fully optimized geometry.

$^b$The bandgap calculated based on the optimized geometry with $\phi$ constrained at zero degree.

Meijer et al. suggested that the difference in donor–acceptor strength of the different units in polymer 6 and 7 might reduce the bandgaps, where the functionalized phenylene units acts as electron donors and the electron deficient pyrazine units act as acceptors. However, polymers based on donor-acceptor units usually have narrow bands due to the weak interactions between the frontier orbitals of the donor and acceptor units. For the model polymer 7, our calculated
width of the HO band is only around 0.3-0.4 eV, and that for LU band is about 1.00 eV. As shown by the band plots in Figure 7.1, the HO band of the model polymer 7 is very narrow which is due to the small inter unitcell overlap as reflected by the crystal orbitals (CO) shown in Figure 7.2. The HOCO is close to the HOMO of the isolated donor unit. The weak interactions originate from the large energy difference of the HOMO of the donor and acceptor units, which generally lead to low bandwidth. The calculated energy difference between the HOMOs of the donor and the acceptor units is as large as 4.38 eV, leading to weak coupling and a small BW.\textsuperscript{2,15}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{7_8b.png}
\caption{The band structures of 7 and 8b. The unit of k is defined as $\pi/a$, where “a” is the length of the translation vector along the polymer chains.}
\end{figure}
Polymers with bandgaps smaller than 1.00-1.50 eV are usually considered as low gap polymers. In order to realize low bandgap polymers, we propose a set of ladder-like polymers based on pyrazine as presented in Chart 7.2, which are likely feasible for synthesis.

**Chart 7.2.** The illustration of the chemical structures of the proposed ladder-like polymers.

8a, R=H

8b, R=CH₃

The common features of these polymers are the electron donating substituents on the pyrazine backbone, and the secondary linkages between unit cells through weak interactions instead of chemical bonds. In polymers 8 and 9, the secondary linkages between neighboring units are two N···H and O···H hydrogen bonds, respectively. The synthesis of the monomer of 8 has been
described by Tour et al.\textsuperscript{8} The R groups in \textbf{8b} provide an opportunity to functionalize the polymers improving solubility. Our PBC calculations at the B3LYP/6-31G(d,p) level indicate that both of the two polymers prefer planar structures. The performance of our theory level has been validated by finding a good agreement between the optimized geometries and the crystal structures of the dimers of \textbf{8} and \textbf{9}. Both the calculated and X-ray structures of the two dimers indicate planar geometries, which are consistent with the planar structure of these polymers.

The calculated bandgaps are listed in Table 7.3. The proposed polymers show bandgaps significantly smaller than those of the previously reported polymers \textbf{1}, \textbf{2}, \textbf{3} \textbf{4}, \textbf{5} and \textbf{6}. The low bandgaps of \textbf{8} and \textbf{9} can be attributed to three factors.

\textbf{Table 7.3.} The calculated bandgaps (in eV) of the proposed ladder-like polymers. The theory levels are B3LYP/6-31G(d,p) for \textbf{8a}, \textbf{8b} and \textbf{9}, and B3LYP/6-31G(2d,p) for \textbf{10} under PBC condition.

<table>
<thead>
<tr>
<th></th>
<th>\textbf{8a}</th>
<th>\textbf{8b}</th>
<th>\textbf{9}</th>
<th>\textbf{10}</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textbf{E}_g</td>
<td>1.37</td>
<td>0.88</td>
<td>1.55</td>
<td>1.65</td>
</tr>
</tbody>
</table>

Planarity of course improves conjugation and BW, and generally reduces the bandgap. However, as discussed before for model polymer \textbf{7}, planar geometry alone is not sufficient to reduce the gap below 2.0 eV. As shown in Figure 7.2, the highest occupied crystal orbital (HOCO) and the lowest unoccupied crystal orbital (LUCO) of \textbf{8} and \textbf{9} show interesting features.
Figure 7.2. The orbital diagram of HOCO (at k=0) and LU CO (at k=0) of the repeat units for PBC calculations.
For the HOCO, there are nodes at the nitrogen in the rings, and for the LUCO, there is significant electron density on nitrogen. Therefore, the relatively large electronegativity value of nitrogen only lowers the LUCO, but does not affect the HOMO, overall reducing the gaps. Moreover, the π-electron donating ability of the amino or hydroxyl groups increases the HOCO levels as manifested by the nodes between \( \text{NH}_2 \) (or \( \text{OH} \)) and the rings, further decreasing the bandgaps.

Beside their small bandgaps, the proposed polymers 8 and 9 show significantly larger BW (around 1.20 eV and 1.90 eV for the HOMO and LUMO bands, respectively) than the ladder-like polymers 5 and 6, which is reflected by the HOCO and LUCO diagrams as depicted in Figure 7.2, and by the large band dispersions shown in Figure 7.1 for 8b.

In addition, we also notice that the bandgap of 0.88 eV for 8b is much smaller than that for 8a. Time dependent DFT (TDDFT) is often considered as a more accurate approximation for excitation energies. Our time dependent B3LYP calculations for 8b show that the small HOCO-LUCO gap agrees well with the lowest allowed singlet excitation energy. It has been suggested that the electron donating abilities of alkyl substituents on polythiophene chains affect the energy levels of HOCO and LUCO.\(^{16}\) In this case, the overall gap reduction, as shown in Figure 7.3 is significant and amounts to 0.5 eV.

\[
\begin{align*}
-4.04 \text{ eV} & \quad -2.67 \text{ eV} \\
-2.58 \text{ eV} & \quad -3.45 \text{ eV}
\end{align*}
\]

8a 8b

**Figure 7.3.** The relative positions of the HOCO (at k=0) and LUCO (at k=0) levels of 8a and 8b.
Planarity can also be realized through the donor-acceptor C-S···N interactions, where the σ lone pair of the sp² hybridized N interacts with the unoccupied σ* orbital of the S–OH bonds. Such nonbonded interactions widely occur in compounds containing divalent sulfurs, and have been analyzed by X-ray structures and theoretical calculations.¹⁷ The structure of the proposed polymer based on such interactions is illustrated by 10 in Chart 7.2. The geometry optimized at B3LYP/6-31G(d) level under PBC condition indicates a planar structure for 10. The calculated nonbonded S···N distance is 2.554 Å much smaller than the sum of van der Waals distance of sulfur and nitrogen, indicating strong intramolecular S···N(sp²) interactions. It is noticed that the HOCO and LUCO orbital patterns (see Figure 7.2) of polymer 10 are very similar to those of polymer 8 and 9. Therefore, the relatively low bandgap of 1.65 eV obtained for 10 can also be attributed to the planar structure and the specific HOCO and LUCO patterns.

In summary, we propose a set of ladder-like pyrazine polymers which show significantly lower bandgaps than PPP and the corresponding nitrogen heterocyclic polymers previously reported. The ladder-like connectivity between unit cells are the intramolecular hydrogen bonds or nonbonded S···N intercalations. The low bandgaps of the proposed polymers is attributed to the planarization of the polymer chains, the specific HOCO and LUCO patterns and the electron releasing substitutes of amino groups and hydroxyl groups. The proposed polymers 8b shows a bandgap smaller than 1.00 eV due to the strong electron donating property of methyl groups.
Acknowledgement

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References


CHAPTER 8

LADDER-TYPE POLYENAZINE BASED ON INTRAMOLECULAR S•••N INTERACTIONS: A THEORETICAL STUDY OF A SMALL BANDGAP POLYMER*

8.1. Introduction

The search for low bandgap polymers has been of considerable interests to chemists and physicists. Most of the conducting or semiconducting polymers are composed of π conjugated systems. In order to achieve low bandgap polymers (usually smaller than 1.50 eV\(^1\)), a variety of strategies have been proposed, for instance building ladder polymers, incorporating electron donor and acceptor segments in the polymer backbone.\(^2\) For π-conjugated polymers, the bandgap depends on the extent of the band dispersion of the orbitals. Larger π-band dispersion is usually accompanied by higher mobility and smaller bandgaps. Building ladder-type π-conjugated polymers can be an effective way to reinforce the frontier orbital overlap between neighboring unit cells, which reduces the bandgaps. A number of ladder-type semiconducting polymers have been designed such as thienoacene,\(^3\) polyacene,\(^4\) and ladder-type Poly(p-phenylene) (PPP)\(^5\). Another strategy for gap reduction is based on the idea that the chemical repeat unit should have an odd number of electrons.\(^6\) Systems with an odd number of electrons in the repeat unit (polyacetylene with its CH unit is a prime example) are not metallic, because of the tendency for bandgap opening and bond length alternation derived from the concept of Peierls’s theorem. The presented system combines the ladder-like topology with an odd number of electrons in the repeat unit of a single system.

Polyacetylene (PA) is one of the “simplest” and most intensely studied archetypical conjugated polymers. Although polyacetylene can achieve metallic conductivity when it is doped with electron donors or acceptors, its intrinsic conductivity lies in the semiconducting range due to a bandgap about 1.5 eV. This bandgap is attributable to the Peierls distortion, the bond length alternation of the carbon–carbon bond distances resulting from the instability of the orbital degeneracy at the Fermi level. In this study, we introduce a new class of ladder-type polyenazine (LPEA, 2) derivatives based on S···N interactions as shown in Scheme 8.1, with the S/N composition of n(4S+4N)+4S+2N where n is the number of repeat unit. The proposed strategy takes advantage of the X-ray structure of molecule 1 (shown in Scheme 8.1) that was reported over twenty years ago, but received little attention. Molecule 1 corresponds to the case of n=0 in term of the S/N composition. One of the characteristic features of the proposed polymers is the nonbonded S···N interactions that lead to a ladder-type structure along the PA backbone. Herein, we investigated by density functional (DFT) calculations the effect of the S···N interactions on the geometrical and electronic properties of the proposed polymers. Our studies demonstrate that the noncovalent S···N intramolecular interactions were able to effectively planarize the polymer chain and enhance the $\pi$ conjugation. Moreover, the $\cdots$S–S···N–N···S$\cdots$ chain forms a $\sigma$-conjugated pathway showing significant band dispersion. The bond length alternation and the band gap of the LPEA are effectively reduced compared to the parent PA.

In a recent study, Houk et al. theoretically explored the potentials of nitrogen-rich oligoacenes as n-channel organic semiconductors. The proposed polymers in this chapter are also nitrogen rich, and they have relatively high electron affinity (EA) in combination with low bandgap,
which are the characteristic parameters related to the stability and electron transport of n-channel polymers.

**Scheme 8.1.** The Chemical Structures of (1) N,N-Bis[2-(5-tert-butyl-3H-1,2-dithiol-3-ylidene)ethylidene]hydrazine; (2) Ladder-type polyenazine (LPEA).

8.2. Computational Methodology

Previous research shows that, for the chain-like polymers, Becke’s half and half hybrid scheme of density functional theory (BHandHLYP) predicts accurate bond length alternations (BLA) while Becke’s three-parameter hybrid functional in combination with Lee-Yang-Parr
correlation functional (B3LYP)\textsuperscript{12} tends to underestimate the BLA. However, the B3LYP bandgaps are more accurate if combined with the BHandHLYP optimized geometry. This trend is shown in Table 8.1, where the calculated BLA and bandgaps of PA are tabulated. The polymers involved in this study resemble the parent PA in terms of the geometrical and electronic structure. Therefore, the B3LYP//BHandHLYP theory level is expected to perform well for the bandgap prediction for the proposed LPEA. In this study, the proposed oligomers and polymers are geometrically optimized at both B3LYP and BHandHLYP levels, and the bandgaps are calculated at the B3LYP level based on the optimized geometries. On the other hand, although experimental values are unavailable to evaluate the theoretical gaps for the proposed polymers, considering the similarity in structure, the predicted values of LPEA are comparable to that of parent PA as long as the same theory levels are used. Consequently, theoretical computations can predict the trends concerning the effects of the ladder structure on the bandgaps of the proposed LPEA.

Table 8.1. Theoretical BLA (in Å) and Bandgaps (E\textsubscript{g}) (in eV) of Polyacetylene.

<table>
<thead>
<tr>
<th></th>
<th>BLA\textsuperscript{a}</th>
<th>HOMO-LUMO\textsuperscript{b}</th>
<th>TDDFT\textsuperscript{c}</th>
<th>PBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP</td>
<td>0.055\textsuperscript{11b}</td>
<td>1.10\textsuperscript{11b}</td>
<td>1.12</td>
<td>1.21\textsuperscript{11b}</td>
</tr>
<tr>
<td>B3LYP//BHandHLYP</td>
<td>0.088\textsuperscript{11b}</td>
<td>1.45</td>
<td>1.27</td>
<td>1.68</td>
</tr>
<tr>
<td>expt</td>
<td>0.08-0.09\textsuperscript{13}</td>
<td>1.50\textsuperscript{7}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} BLA is defined as the difference between the long and short CC bonds.

\textsuperscript{b} The E\textsubscript{g} is calculated by linear extrapolation of the highest occupied molecular orbital (HOMO) – lowest unoccupied molecular orbital (LUMO) gaps of oligomers to infinity.

\textsuperscript{c} The extrapolated E\textsubscript{g} based on the excitation energy of oligomers.
Excitation energies for the oligomers are calculated by applying both the time-dependent DFT (TDDFT) and the HOMO-LUMO gaps based on the optimized geometries. The excitation energies and HOMO-LUMO gaps are linearly or quadratically extrapolated as a function of the reciprocal of the total number of π electrons (n_π) to estimate the polymer bandgaps. The polymer bandgaps are also calculated under periodical boundary condition at the same theory level. The basis set convergence is tested with respect to the bandgap calculations. It is shown that the bandgaps have little change from 6-31G(d) to 6-311G(2d). Addition of a diffuse basis function (6-31+G(d)) changed the bandgap only by about 0.01 eV for the title polymer at the B3LYP//B3LYP level. Therefore, the calculations reported in this study are based on the 6-31G(d) basis set.

The HOMO-LUMO gaps, the bandgaps under periodic boundary conditions (PBC) and the EA calculations are performed employing the Gaussian03 program. The SN bonding energy analysis is carried out with NBO3. The dimerization energies for PA and LPEA are calculated using the Crystal 03 package.

8.3. Results and Discussion

Because of the resemblance in the structure of LPEA to the parent PA, we related the structure and properties of the two polymers and discussed how the structural and electrical properties were changed compared to the parent PA.

8.3.1. Noncovalent S···N Interactions and Quasi-ladder Structure

Synthesis of the oligomer 1 has been described and the structure was characterized by X-ray diffraction. It is shown that the S···N contacts in the molecules are around 2.49 Å, which is
significantly shorter than the sum of van der Waals (vdW) radii of sulfur and nitrogen. The molecule is centrosymmetric with a transoid configuration about the N–N single bond. Our calculated bond distances along the polymer backbone are listed in Table 8.2 in comparison with experimental bond distances. The root mean square deviations (rms) are small and the experimental values agree well with the theoretical predictions. The optimized geometry of the molecule indicates a planar structure with an inversion center.

**Table 8.2.** Theoretical Bond Lengths (in Å) of 1 and The Root Mean Square with Respect to the Experimental Values. Numbering Refers to Scheme 8.1.

<table>
<thead>
<tr>
<th></th>
<th>r₁</th>
<th>r₂</th>
<th>r₃</th>
<th>r₄</th>
<th>r₅</th>
<th>r₆</th>
<th>rms</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP</td>
<td>1.359</td>
<td>1.435</td>
<td>1.380</td>
<td>1.415</td>
<td>1.308</td>
<td>1.360</td>
<td>0.014</td>
</tr>
<tr>
<td>BHandHLYP</td>
<td>1.341</td>
<td>1.439</td>
<td>1.357</td>
<td>1.424</td>
<td>1.284</td>
<td>1.365</td>
<td>0.008</td>
</tr>
<tr>
<td>X-raya</td>
<td>1.336</td>
<td>1.429</td>
<td>1.365</td>
<td>1.414</td>
<td>1.293</td>
<td>1.372</td>
<td></td>
</tr>
</tbody>
</table>

a Ref. 8

As shown in Table 8.3, both B3LYP and BHandHLYP predict SN contacts significantly shorter than the van der Waals distance. Strong noncovalent S···N and S···O bonding is frequently found in crystal structures of organic compounds containing divalent sulfur. The formation of the noncovalent S···N or S···O contacts that produce relatively shorter contacts and therefore stronger interactions than typical vdW interactions are generally ascribed to electron donor-acceptor interactions occurring between the sp² lone pairs of nitrogen or oxygen and the unoccupied σ* orbitals of the S-X bonds (X is covalently bonded to S). In molecule 1, the short
intramolecular SN interactions are expected to be strong according to the considerably short SN
distance. To evaluate the SN bonding strength, we calculated the SN interaction energies using
the NBO method which is widely used for donor-acceptor interaction analysis. According to this
method, the extent of the nonbonded interactions can be approximated with the second-order
perturbative stabilization energies, E(2), between the donor orbitals and acceptor orbitals.\textsuperscript{19} The
calculated SN interaction is 14.62 kcal/mol at the B3LYP//B3LYP level. The relatively strong
nonbonded SN interactions are consistent with the good NBO orbital overlap between the
nitrogen lone pairs and the unoccupied $\sigma^*$ orbitals corresponding to the S–S bond as illustrated in
Figure 8.1.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$r_{SN}$ (expt)</th>
<th>$r_{SN1}$\textsuperscript{a}</th>
<th>$r_{SN2}$\textsuperscript{a}</th>
<th>$E1(2)$</th>
<th>$E2(2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.489\textsuperscript{b}</td>
<td>2.515</td>
<td></td>
<td>14.62</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>N/A</td>
<td>2.683</td>
<td>2.836</td>
<td>7.67</td>
<td>4.22</td>
</tr>
<tr>
<td>2</td>
<td>N/A</td>
<td>2.671</td>
<td>2.841</td>
<td>8.02</td>
<td>4.13</td>
</tr>
<tr>
<td>3</td>
<td>N/A</td>
<td>2.671</td>
<td>2.839</td>
<td>8.02</td>
<td>4.16</td>
</tr>
</tbody>
</table>

\textsuperscript{a}$r_{SN1}$ and $r_{SN2}$ refer to the central SN distances.
Figure 8.1. NBO orbital overlap diagram of the unoccupied $\sigma^*$ S–S orbital and the nitrogen $n$ orbital of molecule 1.

When the oligomer size increases, as exemplified by 3 (Figure 8.2, $n=1$ for 2), each SS bond is in close contact with two nitrogen lone pairs as compared to molecule 1, where each SS bond interacts with only one nitrogen lone pair. As shown in Figure 8.2, the NBO orbital overlap diagram indicates that at both ends of the central SS bonds, the $\sigma^*$ S–S orbitals are in good overlap with the nitrogen lone pairs. However, one notes that the corresponding SN distances increase compared to those in molecule 1, and correspondingly the interaction energies are reduced (See Table 8.3). Moreover, we note that the two SN distances alternate with the longer one corresponding to smaller interaction energy. The weakening of the SN bonding can be explained by the fact that the electron accepting ability of the $\sigma^*$ SS bond is reduced after interacting with one nitrogen lone pair, and thus it is less favored to interact with the second nitrogen lone pair. With increasing oligomer size, the SN interactions tend to converge as demonstrated by the trends shown in Table 8.3.
Figure 8.2. The chemical structure of molecule 3 and the NBO orbital overlap diagram of the unoccupied $\sigma^*$ S–S orbital and the nitrogen n orbital.

8.3.2. Electronic Structure of LPEA

As discussed previously, B3LYP//BHandHLYP accurately predicts the bandgap for parent PA. Therefore, we used it to calculate the energy gaps. On the other hand, the bandgaps based on B3LYP geometry are also reported in this chapter for comparison. The energy gaps are calculated using two complementary approaches. The first approach is based on the DFT HOMO-LUMO energy differences and the TDDFT excitation energies of the oligomers containing up to four repeat units defined by 2 in Scheme 8.1. The bandgap of the polymer is obtained by both quadratically and linearly extrapolating the HOMO–LUMO gaps or the excitation energies with respect to the reciprocal of the number of $\pi$ electron along the backbone. Figure 8.3a and Figure 8.3b show the linear extrapolation plots calculated at the level of B3LYP//B3LYP and B3LYP//BHandHLYP, respectively.
Figure 8.3. DFT HOMO-LUMO gaps (diamonds) and TDDFT excitation energies (squares) as a function of $1/n_\pi$, (a) B3LYP//B3LYP level; (b) B3LYP//BHandHLYP. $n_\pi$ is the number of $\pi$ electrons on the polymer backbone. Oligomers up to four repeat units were used. (The linear fits are provided to guide the eye.)

In the second approach, the bandgap is calculated under periodic boundary conditions. The bandgaps obtained with the two approaches are summarized in Table 8.4. We note that the predicted gaps are about 0.33-0.39 eV smaller than those of the parent PA calculated at the same theory level (refer to Table 8.1 and Table 8.4). The B3LYP//BHandHLYP predicts gaps 0.2-0.4
eV larger than B3LYP//B3LYP, just as the case for the parent PA. The linearly extrapolated HOMO–LUMO gaps are smaller than the PBC values, while the quadratic extrapolations are consistent with the PBC calculations. This is because $E_g$ vs $1/n_\pi$ deviates slightly from a linear relationship as the polymer chains approach infinite size.\textsuperscript{20}

**Table 8.4.** Theoretical BLA\textsuperscript{a} (in Å) and bandgaps ($E_g$) (in eV) of LPEA (2).

<table>
<thead>
<tr>
<th></th>
<th>BLA</th>
<th>HOMO-LUMO</th>
<th>TDDFT</th>
<th>PBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP</td>
<td>0.046</td>
<td>0.64(0.82)</td>
<td>0.57(0.60)</td>
<td>0.88</td>
</tr>
<tr>
<td>B3LYP//BH and HLYP</td>
<td>0.080</td>
<td>1.01(1.29)</td>
<td>0.79(1.00)</td>
<td>1.29</td>
</tr>
</tbody>
</table>

\textsuperscript{a} BLA is defined as $(r_3-r_4+r_5-r_6+r_7-r_8)/3$. Numbering refers to Scheme 8.1.

\textsuperscript{b} The values in parenthesis correspond to quadratic extrapolation.

For the parent PA, the calculated BLA is 0.055 Å and 0.088 Å at B3LYP and BH and HLYP, respectively. For the ladder-PA, the estimated BLA is 0.046 Å and 0.080 Å (only the CC bonds are counted to estimate the BLA) at the corresponding theory levels. Therefore, we attribute the bandgap reduction to the reduced BLA of the LPEA compared to the parent PA. To buttress the interpretation, we also calculated the bandgaps of a model polymer as shown in Scheme 8.2, in which the dithiol groups are replaced by the standard CH bonds, while the other geometrical parameters are kept same as the optimized geometries of the ladder PA. In this model we kept the BLA fixed, and the B3LYP calculated gap of 0.91 eV is almost the same as the gap of the LPEA at the same theory level (0.88 eV).
**Scheme 8.2.** Model Polymer (4) Obtained by Replacing the Dithiol Groups of the Optimized PLA(2) with CH Bonds.

The EA of the polymer is estimated using the same oligomers as those for the evaluation the bandgaps. The linear plot of the oligomer EA as a function of $1/n_\pi$ is shown in Figure 8.4. The estimated value of 3.75 eV is higher than 3.0 eV, which suggests a practical minimum value for n-type semiconductors. At the same time, the calculated EA is below 4.0 eV that is suggested as an upper limit for the stability of the system against common reducing agents. Therefore, the proposed ladder polymer might be considered as a potential n-type semiconductor. The reason for the relative high EA is the relatively high electronegativity of nitrogen in the polymer backbone.
Figure 8.4. Electron affinity calculated by B3LYP//B3LYP, as a function of the reciprocal of the number of π electrons. (The linear fit is provided to guide the eye.)

To elucidate the electronic structure of the ladder polymer, the band structure is presented in Figure 8.5. By inspecting the orbitals, we find that the valence band and conduction band correspond to the extension of the π orbitals of the backbone containing carbon and nitrogen, with little participation from the sulfur π–lone pairs. The interesting finding is about the bands along the weakly bonded linkages forming a ···S–S···N–N···S–S··· chain. We denoted these bands as SN bands. The SN bands are labeled in Figure 8.5 together with the corresponding crystal orbitals (COs) at the Γ point of the Brillouin zone. As we discussed previously, the n orbitals on nitrogen can interact with σ∗ orbitals of the S–S bonds, leading to SN band dispersion. Actually, we find that the occupied SN band (the HOCO-5) indeed has a dispersion of about 0.3 eV. This is small relative to the π-band in polyacetylene (~5 eV) but significantly larger than expected.
from vdW interactions only. As shown by the corresponding orbital, this SN band is composed of $\sigma^*$ orbitals of the S–S bonds and the n orbitals on nitrogen. The significant dispersion of the SN bands further indicates relative strong SN interactions.

**Figure 8.5.** Band structure of the LPEA (2) calculated at B3LYP//B3LYP level. Five highest occupied and five lowest unoccupied bands are shown. The orbitals corresponding to the SN bands are shown at the $\Gamma$ (k=0) point. (X: k=$\pi$/a). The Fermi level, $E_F$, is near -4.0 eV.
One question remains that, since the n orbitals of nitrogen is usually localized, the mixed orbitals of n and σ* should be localized on the N···S–S···N segments, instead of extending along the polymer chain. Actually, the n orbitals on nitrogen interact through-space between the two neighboring nitrogen atoms. Correspondingly, a σ conjugated pathway opens up along the polymer chain. However, the two bands near E_F remain π-type. Consequently, it appears that the reduction of the bandgap can be interpreted in this system as follows: The ladder topology due to the SN chains provides a reduced bond alternation that in turn leads to a smaller bandgap than in the parent PA.

8.3.3. Dimerization Energy

In the ground state, the structure of PA is in a bond length alternation pattern due to a Peierls distortion. The energy barrier between the BLA structures and the hypothetical structure with uniform bond length has been of great interest, since it is related to the formation of solitons and hence the electrical and magnetic properties of PA and related systems. This energy barrier is called dimerization energy.\textsuperscript{22} Our B3LYP calculation shows an energy barrier of 0.32 kcal/mol for each unit cell containing two carbon atoms, which is close to the value by MP2 calculations.\textsuperscript{23} Herein, we explore the energy barrier for the LPEA and compare it with that of PA. For both PA and LPEA, as shown in Scheme 8.3, the higher energy geometry corresponds to the structure with high symmetry of \textit{Pm}2\textit{m} in terms of line group. However, for LPEA, exactly uniform bond length can not be obtained because of the hetero nitrogen atoms and the unit cell configuration. The optimized geometry parameters with \textit{Pm}2\textit{m} symmetry are listed in Table 8.5. The bond length alternation of 0.011 Å of the \textit{Pm}2\textit{m} structure is highly reduced compared to
0.055 Å of the optimized equilibrium geometry. The optimized $Pm2m$ geometry is 2.92 kcal/mol higher in energy than that calculated for the optimized equilibrium geometry. The unit cell of the LPEA is nine times larger than that of the parent PA in the sense of the number of nitrogen and carbon atoms in the polymer backbone. Therefore the total energy per unit cell of LPEA divided by nine leads to an energy barrier of 0.33 kcal/mol per two $\pi$-electrons in the main chain. This barrier happens to be same as that of the parent PA at the same B3LYP level.

**Scheme 8.3.** Structure of LPEA with $Pm2m$ Symmetry.

![Scheme 8.3](image)

**Table 8.5.** B3LYP Calculated Bond Distances$^a$ and BLA in (Å) of the $Pm2m$ LPEA (5).

<table>
<thead>
<tr>
<th></th>
<th>$r_1$</th>
<th>$r_2$</th>
<th>$r_3$</th>
<th>$r_4$</th>
<th>$r_5$</th>
<th>$r_6$</th>
<th>$r_7$</th>
<th>$r_8$</th>
<th>$r_9$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.397</td>
<td>1.412</td>
<td>1.385</td>
<td>1.340</td>
<td>1.323</td>
<td>1.340</td>
<td>1.386</td>
<td>1.412</td>
<td>1.397</td>
</tr>
</tbody>
</table>

$\text{BLA} = \frac{[(r_2-r_1) + (r_2-r_3) + (r_8-r_7) + (r_8-r_9)]}{6} = 0.011$

$^a$ Numbering refers to Scheme 8.3.
8.4. Conclusions

We proposed a class of ladder-type polyenazine where the ladder is stabilized by intramolecular noncovalent SN interactions. Both the B3LYP//B3LYP and B3LYP//BHandHLYP calculations indicate strong SN interactions in the oligomers according to an NBO analysis. The intramolecular SN interactions account for the planar ladder structure of the proposed polymer. The calculations indicate that the bandgap of the new LPEA is 0.33-0.39 eV smaller than the value of the parent PA (PBC values). We attribute the narrower bandgaps to the reduced BLA of the ladder-PA arising from the SN interactions. The calculated EA is high (3.75eV), and it lies in the range suitable for n-type semiconductors. The band structure analysis shows that the valence band and conduction band are composed of the $\pi$ orbital of the backbone containing nitrogen and carbon. We found a $\sigma$-conjugated pathway along the $\cdots$S–S $\cdots$N–N $\cdots$S–S $\cdots$ chain, which is formed by the unoccupied $\sigma^*$ orbital of S–S bonds and the n orbital of nitrogen. The calculations at the same theory level of B3LYP indicate that the dimerization energy of LPEA is nearly same as that of the parent PA. The small barrier indicates that it might be possible to further reduce the gap by further reducing the bond alternation by properly designed repeat units.

Acknowledgement. Financial support from the National Science Foundation (Grant No. DMR-0331710) is gratefully acknowledged. Support by GridChem is acknowledged for computer time.
References


15 NBO Version 3.1, Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F.


CHAPTER 9

MOLECULAR ACTUATORS DESIGNED WITH S::N(sp²) HEMIBONDS ATTACHED TO A CONFORMATIONALLY FLEXIBLE PIVOT*

9.1. Introduction

The design of molecular machines has been an intriguing challenge for chemists to mimic actions of biological motors.¹ One of the most interesting subjects is to develop actuators or artificial muscles, which simulate some aspect of the contractions associated with skeletal muscles. Various actuation mechanisms are based on the ability of the actuator materials or assemblies to transduce optical,² electrical³ or chemical⁴ stimulus into mechanical work through dimensional response. The advantages and limitations of the reported artificial muscles have been summarized by Baughman and strategies to improve the performance were suggested.⁵

Electro-active materials which attracted much interest as electromechanical actuators include conducting polymers such as polypyrrole,⁶ polyaniline,⁷ and polythiophene⁸ and helical structures⁹. The operating principle of this class of redox-active materials is based on the intercalation of dopants and counterions by inducing a volume change of the polymer matrix by swelling. The major disadvantage of this bulk mechanism is that the actuation frequency is diffusion limited by the counterion flux. In order to overcome this limitation, alternatives have been discovered where the actuation mechanism relies on the intrinsic properties of the actuator materials as e.g. for polyacetylene and carbon nanotubes.¹⁰ The linear strain (s) is defined as the

ratio of the change ($\Delta l$) to the length ($l$) of polymer chains or nanotube sheets as a function of injected charge ($q$):

$$s(q) = \frac{\Delta l(q)}{l}. \quad (9.1)$$

For the intrinsic mechanism $s$ is small since the dimensional change in this case is due to the contraction or expansion of covalent bonds upon electrochemical reduction and oxidation. With this in mind, chemists are interested in constructing actuators driven by conformational changes at the molecular level. Promising systems include thiophene-fused [8]annulene,$^1$ $\pi$-stacking thiophene oligomers,$^2$ and crown-annelated oligothiophenes.$^3$ PVDF (poly-(vinylidene fluoride)) based nanoactuators have been investigated both experimentally$^4$ and computationally$^5$ showing large lattice strains (experimentally often characterized by the percent change of film thickness) associated with phase transformations of the material. Based on a different mechanism rotaxane-based molecular shuttle-actuator is capable of reversible mechanical switching driven by chemical, electrochemical or photochemical stimuli in solution.$^6$

In this chapter we introduce a novel strategy to design molecular actuators based on a floppy biphenyl-like (2-phenylpyridine, 2PPy) pivot and redox-controlled $S\cdots N$ interactions. The proposed general architecture and actuation process is illustrated in Chart 9.1. The building block is composed of three components: an electro-active part, a movable rigid beam carrying the load (shaded in Chart 9.1) and a 2PPy pivot. The first two parts are bridged through the 2PPy pivot. The electroactive component and the 2PPy pivot are built of 2-(2-(methylsulfanyl)phenyl)pyridine (MSPPy, 3) in our design. The divalent sulfur and the proximal $sp^2$ hybridized nitrogen in MSPPy (3) play the role of the electro-active component through the
formation of a $S::N$ hemibond after a one-electron oxidation of the actuating unit which in turn results in the planarization of 2PPy, which transduces the forces into the rigid beams leading to a closed configuration as shown in Chart 9.1.

![Chart 9.1. Schematic drawing of the proposed actuator composed of an electro-active MSPPy (3) pivot and linear rigid beams (shaded). The shaded rectangles indicate the attached groups that rotate relative to one another.]

It is well known that divalent sulfur compounds can be easily one electron oxidized giving rise to radical cations essentially localized on sulfur due to the relatively low ionization potentials of these molecules.\textsuperscript{17} The S-centered radical cations can be stabilized by a partner atom bearing an appropriately oriented electron lone pair allowing the formation of a two-center(2c) three-electron (3e) hemibond,\textsuperscript{18, 19} or $2\sigma/1\sigma^*$ bond, denoted as $S::X$ in this study (X is the atom providing lone pair electrons).\textsuperscript{2c/3e} hemibonds can be qualitatively described by the orbital diagram of the prototype $[\text{H}_2\text{S}::\text{S H}_2]^+$ system as depicted in Chart 9.2.\textsuperscript{20}
The two p-orbitals on sulfur, one bearing the cation radical and the other bearing the lone pair of a neutral molecule, overlap resulting in one doubly occupied bonding orbital and one singly occupied antibonding orbital. Therefore, the cation radical is stabilized through mixed valence bonding in the dimer. In an analogy to the prototypical hemibond in $[\text{H}_2\text{S} \cdot: \cdot \text{SH}_2]^{2+}$, in this study we propose an intramolecular $\text{S} \cdot: \cdot \text{N}(sp^2)$ hemibond in MSPPy ($3^{2+}$) which acts as an electro-active hinge.

The other feature of the proposed design is the flexibility of the $\alpha–\alpha'$ connection of the 2PPy scaffold, which acts as a pivot to transduce the forces generated by the formation of a $\text{S} \cdot: \cdot \text{N}$ hemibond to the rigid beams. It is well known that biphenyl and analogous molecules are quite floppy with respect to the torsion angle along the bridging $\text{C}_\alpha–\text{C}_{\alpha'}$ bond.$^{21,22,23}$

As is discussed in the following sections, the expected dimensional response of the designed actuators is high. In this study, the geometrical and electronic properties of the proposed molecular actuators are explored with density functional theory (DFT) and ab initio (MP2) calculations. The performance of the theory level used in the chapter is evaluated through the comparisons with experiments whenever possible. The $\text{S} \cdot: \cdot \text{N}$ hemibond strength is compared to
other well studied 2c/3e hemibonds involving S-centered radical cations. The strategies to modify the 2PPy pivot are discussed in order to improve the performance of the proposed electrochemical actuators including molecular springs composed of several electro-active units.

9.2. Computational methodology

Full geometry optimizations\textsuperscript{24} were carried out by using the Becke’s three parameter (B3) hybrid exchange functionals combined with Lee-Yang-Parr(LYP) correlation functionals (B3LYP)\textsuperscript{25}. The performance of B3LYP for 2c/3e hemibonds has been evaluated showing good agreement with high level calculations including Møller-Plesset perturbation theory of the second order (MP2).\textsuperscript{26} Moreover, the calculated (N.:N)\textsuperscript{+} distance in \ref{fig:hemibond} is in good agreement with the x-ray structure. On the other hand, a large number of theoretical studies on the 2c/3e S.:X systems have been reported using BH&HLYP functionals, which include half Hartree-Fock exchange, half Slater exchange, and a LYP correlation functional.\textsuperscript{27} Therefore, we additionally used BH&HLYP for comparison with the B3LYP calculations. The fully optimized structures were examined by frequency calculations at the same theory level to confirm that they are local minima. We also use the hybrid meta-generalized gradient M05-2X functional\textsuperscript{28} which has been recently developed aiming to account for correlation energies at medium and long range. The performance of this functional has been evaluated for various systems including the difficult boron-nitrogen coordinate covalent bond strength\textsuperscript{29}, closed-shell dimers\textsuperscript{30} and the energetics of bond dissociation\textsuperscript{31}. Previous studies suggest that the hemibond energies and distances display little basis set dependence.\textsuperscript{32} The effect of basis set on the optimized the geometric parameters are also evaluated in this study, indicating that the modest basis set of 6-
31G(d) gives very similar results when compared with the larger basis sets such as 6-31G(2d,p). Therefore, all fully optimized geometries in this study are calculated using the 6-31G(d) basis set. As all of the hemibonding systems in this study were open shell (S=1/2), we checked the spin contamination for the calculations with unrestricted (U) methods. The square of spin angular momentum is very close to the ideal value of 0.75 for all of the reported calculations with UB3LYP, UBH&HLYP and UM05-2X methods. All potential energy scans (PESs) are fully relaxed unless specific constraints are explicitly stated.

Natural bond orbital (NBO) analysis was performed by employing the NBO 3.1 program\textsuperscript{33} for the evaluation of electron donor-acceptor interactions.

Mayer’s bond order (MBO) analysis was performed using the program APEX4\textsuperscript{34} based on the single determinant wavefunction built upon the Kohn-Sham orbitals in DFT. According to Mayer, the ab initio bond index between atom A and B can be defined as\textsuperscript{35},

\[
B_{AB} = 2 \sum_{\mu \in A} \sum_{\nu \in B} \left[ (P^\alpha S)_{\mu \nu} (P^\alpha S)_{\nu \mu} + (P^\beta S)_{\mu \nu} (P^\beta S)_{\nu \mu} \right]
\]  

(9.2)

Where \(S\) is the overlap matrix; \(P^\alpha\) and \(P^\beta\) are the density matrix for spin \(\alpha\) and spin \(\beta\), respectively.\textsuperscript{36, 37}

In addition to the bond order indices, we evaluated the strength of the intramolecular 2c/3e hemibonds by employing the conformational method,\textsuperscript{38} which has been applied for evaluating the intramolecular hydrogen bonding energies.\textsuperscript{39} In this study, the intramolecular bonding is switched on (structure \(3^{++}\)) and off (structure \(4^{++}\)) through the rotation around the bridging C1C1′ bond as shown in Chart 9.3. The 2c/3e hemibond energies are estimated by calculating the energy difference between \(3^{++}\) and its conformer \(4^{++}\). The electronic delocalization energy and
steric repulsion might also contribute to the energy difference between the two conformations. However, such contributions are expected to be a minor factor compared to the 2c/3e hemibonds, if, for the conformer $4^{+}$, the dihedral angles ($\omega$) between H$_3$CS$^-$ group and the phenyl ring were constrained at the same values as that of the fully optimized geometry of structure $3^{+}$. Detailed discussion is presented in the following sections. Three theory levels including B3LYP, MP2 and CCSD are used for the energy calculations of the isomers based on the geometries optimized at B3LYP/6-31G(d) level. The MP2 calculation is based on restricted Hartree-Fock reference orbitals (ROMP2).

![Chart 9.3](image)

**Chart 9.3.** The structures of the neutral (3) and the oxidized ($3^{+}$) MSPPy and its conformer ($4^{+}$). The latter is used for bond energy analysis, see text.

9.3. Results and discussion

2c/3e S::X hemibonds can be established not only between molecules but also within a molecule when cationic radical S-center interacts with a nearby atom (X) bearing an appropriate lone pair in the same molecule.$^{40}$ In accordance with the simple orbital overlap justification, the formation of S::X hemibonds is favored for the molecular configurations which allow the
alignment between the sulfur 3p-orbital and the lone pair orbital on atom X. Two typical cases are shown in Chart 9.4: 1,5-dithiacycloocane\textsuperscript{41} (DTCO, 5\textsuperscript{+}) and 3-methythio propylamine\textsuperscript{42} (3-MTPA, 6\textsuperscript{+}) both of which form strong 2c/3e hemibonds after one-electron oxidation. The relatively strong bonding manifests itself in the high stability of their radical salts as established by ESR measurements in acetonitrile solution\textsuperscript{41b, 43} as well as the low oxidation potentials measured by cyclic voltammetry in acetonitrile\textsuperscript{44}. Moreover, intramolecular hemibonds are expected to be kinetically more stable compared to the intermolecular ones, since the molecular framework helps to hold the two atoms forming hemibond in proximity of each other. For instance, some intramolecular (N\textsuperscript{∶}N)\textsuperscript{+} hemibonds have been characterized by X-ray diffraction.\textsuperscript{45} An example is shown in Chart 9.5, in which the (N\textsuperscript{∶}N)\textsuperscript{+} hemibond in N,N-trimethylene-syn-1,6:8,13-diimino[14]annulene (7\textsuperscript{+}) has an unusual equilibrium NN distance of 2.160 Å.\textsuperscript{46}

![Chart 9.4. The structures of the radical cations of DTCO (5\textsuperscript{+}), and 3-MTPA (6\textsuperscript{+})](image-url)
Inspired by these examples, we suggest molecular actuators driven by the reversible formation and disassociation of \(\text{S} \ldots \text{N}\) hemibond in a redox process. \(sp^3\) hybridized nitrogen \((N(sp^3))\) provides a \(\sigma\) lone pair, as for example \(\text{NH}_3\). \(sp^2\) hybridized nitrogen \((N(sp^2))\) can provide a \(\sigma\) lone pair, as for example pyridine, or \(N(sp^2)\) can be a \(\pi\) electron donor, as for example in pyrrole. Our calculations indicate that \(\text{NH}_3\) and pyridine forms a three electron hemibond with the S-centered radical cation of \(\text{H}_2\text{S}^{+}\). As shown in Chart 9.6, the optimized \(\text{S} \ldots \text{N}\) hemibond distances are very similar for the two systems, \([\text{H}_3\text{N} \ldots \text{SH}_2]^+ (8^+)\) and \([\text{C}_5\text{H}_5\text{N} \ldots \text{SH}_2]^+ (9^+)\). In this study, we classify the \(\text{S} \ldots \text{N}\) hemibonds into two types: \(\text{S} \ldots N(sp^3)\) and \(\text{S} \ldots N(sp^2)\). These are illustrated as \(8^+\) and \(9^+\) in Chart 9.6. As will be seen in the following sections, the hemibonds involved in the design of actuators belong to the \(\text{S} \ldots N(sp^2)\) type.
Chart 9.6. The optimized geometries of \([\text{H}_3\text{N}::\text{SH}_2]^+ (8^+)\) and \([\text{C}_5\text{H}_5\text{N}::\text{SH}_2]^{++} (9^{++})\) at the B3LYP/6-31G(d) level.

9.3.1. The S::N\((sp^2)\) hemibond in the oxidized MSPPy \((3^{++})\) and C-S::N noncovalent bonding in the neutral state \((3)\)

For the MSPPy hinge \((3)\), the torsion angle \(\phi\) (C6-C1-C1'-'C6') along the bridging C1C1' bond (see Chart 9.3 for the labeling) is the characteristic geometry parameter related to the molecular motion in a redox actuation process. As shown in Table 9.1, the fully geometry optimization with different DFTs indicates that the dihedral angles are around 40° at the neutral state \((3)\) due to steric repulsions, while in the one electron oxidized state \((3^{++})\), the configuration becomes nearly planar. Therefore, the MSPPy \((3)\) hinge is electro-active with respect to the rotations along the C1C1’ bond of the 2PPy pivot.

According to the fully optimized geometries with various DFTs, the radical cation of MSPPy \((3^{++})\) shows that \(\phi\) is close to zero (see Table 9.1) and the S···N distance of 2.411Å is far below the sum of van der Waals radii of sulfur and nitrogen. These geometrical characteristics clearly indicate that an intramolecular S::N\((sp^2)\) hemibond has been formed. The molecular orbital (see Figure 9.1) displays strong bonding overlap between the sulfur and the nitrogen. Additionally,
the Mulliken atomic spin density is 98% localized on sulfur and nitrogen, further indicating that the \( S \cdot N(sp^2) \) hemibond is localized between the sulfur and the nitrogen.

**Table 9.1.** The calculated torsion angles \( \phi \) (in degrees) (see Chart 9.3 for the labeling) in the MSPPy (3) and MTTPPy (11) hinge in the neutral and one-electron oxidized state. The 6-31G(d) basis set is used for all calculations

<table>
<thead>
<tr>
<th>Oxidation state</th>
<th>MSPPy (3)</th>
<th>MMTPPy (11)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
<td>3(^{+})</td>
</tr>
<tr>
<td>B3LYP</td>
<td>36.29</td>
<td>2.18</td>
</tr>
<tr>
<td>BH&amp;HLYP</td>
<td>40.93</td>
<td>1.72</td>
</tr>
<tr>
<td>M05-2X</td>
<td>40.98</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>11(^{+})</td>
</tr>
<tr>
<td>B3LYP</td>
<td>56.70</td>
<td>1.44</td>
</tr>
<tr>
<td>BH&amp;HLYP</td>
<td>58.34</td>
<td>1.45</td>
</tr>
<tr>
<td>M05-2X</td>
<td>55.93</td>
<td>0.85</td>
</tr>
</tbody>
</table>

**Figure 9.1.** The bonding molecular orbital of the hemibond (corresponds to the \( \sigma \) orbital in Chart 9.2) of \( S \cdot N(sp^2) \) in the radical cation of MSPPy (3\(^{+}\)) at the B3LYP/6-31G(d) level.

We also calculated the Mayer’s bond order (MBO) to characterize the strength of the \( S \cdot N(sp^2) \) hemibond. Bridgeman et al. have applied the MBO index to characterize the bond strength for both the two center chemical bonds and multicenter bonding including the weak
The MBO index for the intramolecular S:N(sp²) hemibond in MSPPy (3⁺⁺) is listed in Table 9.2. In order to assess the strength of the intramolecular S:N(sp²) hemibonds, the bond orders of several typical N:N (7⁺⁺), S:S(5⁺⁺, 10⁺⁺) and S:N(sp³) (6⁺⁺) hemibonds were also provided. The formation of the Me₂S:SMe₂ dimer (10⁺⁺) has been experimentally confirmed by mass spectroscopy.

<table>
<thead>
<tr>
<th>Compound</th>
<th>10⁺⁺</th>
<th>7⁺⁺</th>
<th>5⁺⁺</th>
<th>6⁺⁺</th>
<th>3⁺⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of contact</td>
<td>Me₂S:SMe₂</td>
<td>S:S</td>
<td>N:N</td>
<td>S:S</td>
<td>S:N(sp³)</td>
</tr>
<tr>
<td>MBO</td>
<td>0.4255</td>
<td>0.3022</td>
<td>0.4343</td>
<td>0.3793</td>
<td>0.3648</td>
</tr>
<tr>
<td>Stretching frequency</td>
<td>229</td>
<td>399/481ᵃ</td>
<td>222</td>
<td>265 (288)ᵇ</td>
<td>296</td>
</tr>
<tr>
<td>r(S:S), r(S:N) or r(N:N)</td>
<td>2.190</td>
<td>2.946</td>
<td>2.160ᶜ</td>
<td>2.844</td>
<td>2.574 (~2.50)ᵇ</td>
</tr>
</tbody>
</table>

ᵃ The N:N stretching modes strongly couple with other vibrations.
ᵇ Ref. 42
ᶜ Ref. 46

The bond order indices indicate that the strength of the S:N(sp³) hemibond in MSPPy (3⁺⁺) is comparable to that of the typical S:N(sp³) hemibond in 3-MTPA (6⁺⁺), and it is a somewhat weaker than the symmetric S:S hemibonds are in Me₂S:SMe₂⁺⁺ (10⁺⁺) and DTCO (5⁺⁺). The vibrational frequencies dominated by the S:X stretching vibrations are also listed for the radical
cations of these compounds in Table 9.2. The calculated unscaled frequency is in fair agreement with the experimental value for 3-MTPA (6⁺⁺). The similar wavenumbers further indicate that the bond strengths of the S::N(sp²) hemibond in MSPPy (3⁺⁺) are comparable to the typical S::N(sp³) hemibond in 3-MTPA (6⁺⁺). The calculated slightly larger wavenumber for 7⁺⁺ is due to the coupling of the N::N stretching with vibrations of the attached framework. As shown in Table 9.2, the calculated N::N distance for 7⁺⁺ is in good agreement with the X-ray structure further confirming the reliability of this level of theory for these systems. The calculated S···N distance in MSPPy (3⁺⁺) is a little longer than that in 3-MTPA (6⁺⁺). All the above evidence indicate that the S::N(sp²) hemibond in MSPPy (3⁺⁺) is relatively strong and is capable of providing the driving forces for the planarization of the 2PPy pivot.

We evaluated the S::N(sp²) bonding energies using the conformational method described in the methodology section. The main structural difference between MSPPy (3⁺⁺) and the conformer (4⁺⁺) is that for the later, the H₃CS− group is positioned far away from the nitrogen heteroatom preventing the formation of an S::N(sp³) hemibond. Secondly, the delocalization energies are different for the two systems. The fully optimized geometry of the conformer (4⁺⁺) indicates that the dihedral angle ω tends to be zero (see Chart 9.3 for the labeling). This is because such planarization favors electron delocalization between the S(3p) orbitals and the π molecular orbitals on the phenyl ring. However, for MSSPy (3⁺⁺) there is a competing effect of forming a S::N(sp²) hemibond, which favors the dihedral angle of 90 degrees and reduces the electron delocalization. In order to evaluate the strength of S::N(sp²) hemibonds using the conformational method, the delocalization effect should be kept at the same level for MSPPy
(3⁺) and the conformer (4⁺). For this reason, the geometries of the conformer (4⁺) were optimized with the dihedral angle ω, constrained to the same value of the MSPPy (3⁺), and the total energies were calculated based on the constrained geometry. In this construction, the energy difference between 3⁺ and 4⁺ mainly arises from the presence and absence of a hemibond, respectively. The estimated S::N(sp²) bonding energies thus calculated are listed in Table 9.3 using the B3LYP and ROMP2 and CCSD methods. All these various theory levels give strong bonding interaction which is in accordance to the large MBO indices obtained for 3⁺.

**Table 9.3.** The S::N(sp²) bonding energies (kcal/mol) in the radical cation of MSPPy (3⁺) approximated by the energy difference between 3⁺ and 4⁺. The geometries for the energy calculations are all optimized at the B3LYP/6-31G(d) level. The dihedral angle ω of 4⁺ is constrained to the same value as that in 3⁺

<table>
<thead>
<tr>
<th></th>
<th>B3LYP/6-31G(d)</th>
<th>ROMP2/6-31G (d, p)</th>
<th>CCSD/cc-pVDZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>E(4⁺)-E(3⁺)</td>
<td>17.73</td>
<td>18.51</td>
<td>22.39</td>
</tr>
</tbody>
</table>

For an efficient molecular actuator, the electroactive components should not be too flexible with respect to the characteristic geometry parameters, such as the torsion angle φ in this study. Otherwise, the actuating function would be lost when the actuator is working against a load. Therefore, we examined the potential energy surface of MSPPy (3⁺) in the one-electron oxidized state. The relevant PES is presented in Figure 9.2 which shows a barrier of ~10 kcal/mol at φ=90⁰.
Figure 9.2. Potential energy scan of the radical cation of MSPPy (3⁺) at the B3LYP/6-31G(d) level. The scanning is along the torsion angle \( \phi \) (in degrees).

We now turn to the electronic and structural properties of the neutral MSPPy (3) molecule. The noncovalent bonding interactions between divalent sulfur and heteroatoms like oxygen and nitrogen have been recognized in many organic compounds. Such noncovalent interactions are schematically described as X–S···Y, where X is covalently boned to S. The formation of the noncovalent X–S···Y contact is generally attributed to the donation of the electrons from the highest occupied \( \pi \) or \( n \) orbitals of Y to the unoccupied \( \sigma^* \) orbitals of the S–X bonds. Inspecting the fully optimized geometry of neutral MSPPy (3), we find a number of geometric indicators for the existence of noncovalent C-S···N interactions, as shown in Table 9.4. First, the S···N distance is 2.86 Å far below the sum of van de Waals radii of sulfur and nitrogen. Second,
the H3CS− group is nearly coplanar with the attached phenyl ring, which allows the alignment between the lone pair orbital of nitrogen and the unoccupied σ* orbital of the S-C bond leading to donor-acceptor interactions between S and N. The non-negligible value of MBO index also indicates the presence of noncovalent C-S···N interactions. The NBO method has been widely used for the noncovalent bonding analysis involving donor-acceptor interactions. The extent of noncovalent interactions can be described with the second order perturbative stabilization energies, E(2). The calculated E(2) is 2.76 kcal/mol (see Table 9.4), which is consistent with the non-negligible bond order index. The C-S···N interactions tends to counteract the steric repulsion and reduce the characteristic dihedral angle of the MSPPy hinge at the neutral state (3), which might impair the magnitude of dimensional change. In order to increase the dimensional response, we further modified the MSPPy (3) hinge aiming for a more open molecular shape in the neural state, as discussed in the following section.

Table 9.4. Geometrical parameters, MBO indices and interaction energy, E(2), between S and N in the neutral MSPPy (3) and the neutral MMTPPy (11) calculated at the B3LYP/6-31G(d) level. See Chart 9.3 for the atomic labeling

<table>
<thead>
<tr>
<th></th>
<th>S···N (Å)</th>
<th>Me-S-C2-C3 (ω) (°)</th>
<th>C6-C1-C1′-C6′ (φ) (°)</th>
<th>MBO</th>
<th>E(2) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSPPy (3)</td>
<td>2.86</td>
<td>22.02</td>
<td>36.29</td>
<td>0.07</td>
<td>2.76</td>
</tr>
<tr>
<td>MMTPPy (11)</td>
<td>3.27</td>
<td>93.05</td>
<td>56.70</td>
<td>0.01</td>
<td>&lt; 0.50</td>
</tr>
</tbody>
</table>
9.3.2. Electronic and structural properties of neutral (11) and oxidized (11⁺) 2-(3-methyl-2-(methylthio)phenyl)pyridine

In order to switch off the nonbonded C-S···N interactions aiming for a more open configuration in the neutral state, we suggest a further modification of MSPPy (3) by introducing a methyl group ortho to the H₃CS− group. This modified hinge leads to MMTPPy (11) which is illustrated in Figure 9.3.

![Chemical structures of MMTPPy (11) and its conformer (12).](image)

Figure 9.3. The chemical structures of MMTPPy (11) and its conformer (12).

According to the fully optimized geometry (See Table 9.4), the torsion angle of the neutral MMTPPy (11) is 56.70°, significantly larger than that of the neutral MSPPy (3). Accordingly, MMTPPy (11) is expected to be more efficient as an actuating molecule. For the neutral MSPPy (3), as shown in Figure 9.4a, N, S–C are nearly aligned, which allows the C–S···N interactions. For the neutral MMTPPy (11), however, the steric repulsion between the two methyl groups prevents the alignment of N, and S–C as shown in Figure 9.4b. As a result, the noncovalent C–S···N interactions are impeded, and the neutral MMTPPy (11) is more open than neutral MSPPy (3). The disappearance of C–S···N interactions in neutral MMTPPy (11) is further confirmed by the negligible S···N MBO index and interaction energy, E(2), as shown in Table 9.4.
Figure 9.4. The fully optimized geometry of (a) neutral MSPPy (3) and (b) neutral MMTPPy (11). Dashed line: the dihedral angle of Me-S-C2-C3 ($\omega$); Solid line: the dihedral angle of C6-C1'-C6' ($\phi$). The calculations are at the B3LYP/6-31G(d) level.

The function of the methyl group as an inhibitor of the nonbonded C–S···N interaction is also reflected by comparing the potential energy surfaces of MSPPy (3) and MMTPPy (11) as shown in Figure 9.5. Due to the prevention of C–S···N interactions and the large steric repulsion between the lone pair of sulfur and nitrogen, MMTPPy (11) displays a much higher barrier than MSPPy (3) with respect to the planar configuration.
Figure 9.5. Potential energy scan as a function of $\phi$ (in degrees) of the neutral MSPPy (3, triangles) and neutral MMTPPy (11, open circles) at the B3LYP/6-31G(d) level.

In the one-electron oxidized state, a $S \cdot \cdot N(sp^2)$ hemibond form, and the MMTPPy ($11^{\ddagger}$) hinge is planarized just as for MSPPy ($3^{\ddagger}$). The strength of this $S \cdot \cdot N(sp^2)$ hemibond can be approximately evaluated with the conformational method using the isomer shown by $12^{\ddagger}$ in Figure 9.3. The estimated $S \cdot \cdot N(sp^2)$ energies at the B3LYP and ROMP2 level are listed in Table 9.5. The calculated hemibonding energies are very close to the corresponding values of MSPPy ($3^{\ddagger}$). However, as shown in Figure 9.6, the potential surface of MMTPPy ($11^{\ddagger}$) shows an energy barrier of 14.5 kcal/mol, which is significantly larger than 10.1 kcal/mol of MSPPy ($3^{\ddagger}$). Therefore, the MMTPPy ($11^{\ddagger}$) is more rigid than MSPPy ($3^{\ddagger}$) in their one-electron oxidized state. A possible reason for that is that as shown in Figure 9.7, at the torsion angle of 90$^\circ$, the
steric repulsion between the two methyl groups prevent effective electron delocalization between the sulfur and the attached phenyl ring for MMTPPy (11').

**Table 9.5.** The S: N(sp^2) bonding energies (kcal/mol) in MMTPPy (11') estimated by the conformational method as the energy difference between 11' and 12'. The geometries for energy calculations are all optimized at the B3LYP/6-31G(d) level. The dihedral angle ω of 12' is constrained to the same value as that in 11'.

<table>
<thead>
<tr>
<th>Method</th>
<th>B3LYP/6-31G(d)</th>
<th>ROMP2/6-31G(d, p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E(12') - E(11')</td>
<td>17.68</td>
<td>18.74</td>
</tr>
</tbody>
</table>

**Figure 9.6.** Potential energy scan of MMTPPy (11') as a function of the dihedral angle φ along the C1C1' bond at the B3LYP/6-31G(d) level.
Figure 9.7. The optimized geometries of (a) MSPPy (3⁺); (b) MMTPPy (11⁺) with the constraint of $\phi = 90^\circ$ at the B3LYP/6-31G(d) level. The optimized dihedral angle is given in degrees.

9.3.3. Actuation simulation

With the finding that MMTPPy (11) is more dimensionally sensitive than MSPPy (3) in a redox process, we build up molecular actuators based on the rotational motion of this electro-active hinge, and simulate the actuation behavior of the proposed actuators. For this purpose, we add “loading beams” to MMTPPy (11) such that the proposed actuators act like a cantilever driven by forces associated with the formation and disassociation of $\text{S} \cdot \text{N}(sp^3)$ hemibonds in a redox process. Two criteria are suggested for the selection of the appropriate beams: (i) The beams should be rigid, and (ii) the electro-active property of the MMTPPy (11) hinge should remain intact after it is connected to the beams. In this study the actuators (13) are constructed as sketched in Figure 9.8 for the actuation simulation. The dimensional response of the actuator can
be described with the openness of the two beams as illustrated in Figure 9.9. The strain \((s)\) is the percentage change of the length of the molecular assembly which is approximately equal to

\[
s = \frac{\left( \sin \frac{\phi_1}{2} - \sin \frac{\phi_2}{2} \right)}{\sin \frac{\phi_1}{2}} \times 100\%
\]  
(9.3)

Where \(\phi_1, \phi_2\) are the C6-C1-C1'-C6' torsion angles of the MMTPPy (11) hinge in the neutral and charged state, respectively.

![Figure 9.8. The structure of the proposed actuators based on MMTPPy (11).](image)

![Figure 9.9. The schematic diagram illustrating the variables in eq. (3).](image)
According to the simulation results shown in Figure 9.10, the torsion angles change from 57.07° at the neutral state (13) to 6.53° in the one-electron oxidized state (13⁺), and the strain without the load is around 88% as obtained from eq. (3). This dimensional response is quite large compared to the electrochemical actuators reported earlier. More importantly, the electro-active property of the MMTPPy (11) hinge remains intact after the connection with the extended beams.

![Diagram of actuator configurations](image)

**Figure 9.10.** The open (reduced) and closed (oxidized) configurations of the proposed actuator (13) optimized at the B3LYP/6-31G(d) level.

As seen from Figure 9.11, in the neutral and the one-electron oxidation state, the actuator (13) shows very similar potential energy surfaces as MMTPPy (11). This further indicates that the electronic properties of MMTPPy (11) are not affected by the beams. Under “push” load, the structure is expected to be below but close to the minimum at $\phi=60^\circ$. Upon oxidation the
molecule will slide to $\phi=0^\circ$. This motion is reversible and is our model of actuation under “push” load. Under “pull” load, the structure is expected to be above but close to the minimum at $\phi=125^\circ$. Upon oxidation the molecule will remain close to this configuration and no actuation would result, unless the angle is under $\phi=90^\circ$. This might be achievable with conformational restrictions. In that case the system would slide down to $\phi=0^\circ$ also reversibly.

**Figure 9.11.** The potential energy scan of 13 (triangles) and $13^+$, (open squares). The scanning is along the torsion angle $\phi$ at the B3LYP/6-31G(d) level.

The actuators 13 shown in Figure 9.10 can be extended by introducing an additional electroactive unit of MMTPPy (11) hinge on the other side of the beams as shown by the structure 14 in Figure 9.12. As the electroactive properties of the MMTPPy (11) hinge remain intact after being connected to the extended arms, each MMTPPy (11) can be envisioned as an
isolated electro-active unit. Thus, a molecular spring can be built up with an array of the electro-active units connected with extended beams. Each unit is expected to work independently but in unison with respect to the response to the electrical stimulus, and thus they jointly contribute to the contraction or expansion of the molecular spring. We performed a quantum mechanical simulation at the B3LYP/6-31G(d) level for the actuator (14) composed of two MMTPPy hinges and three beams as shown in Figure 9.12. The optimized structures are illustrated in Figure 9.12 for the neutral state (14) and the two-electron oxidized state (14\textsuperscript{2+}), respectively. As expected, the electro-active properties of the MMTPPy unit are essentially unchanged in this multicomponent actuator. The torsion angle changes from around 56º to 7º for each unit, which corresponds to a strain value similar to that of the actuator 13.

![Diagram](image)

**Figure 9.12.** The open (reduced) and closed (oxidized) configurations of the proposed actuator constructed with two MMTPPy (11) hinges and three beams. The geometry optimization is at the B3LYP/6-31G(d) level.
Conclusions

Molecular nano-actuators were designed based upon the electro-active molecules MSPPy (3) and MMTPPy (11) proposed in this study. The calculations indicate the formation of S::N \((sp^2)\) hemibonds in their one-electron oxidized states, which results in the planarization of the 2PPy scaffolds of the two molecules. The stretching frequency, molecular geometry and MBO index suggest that the intramolecular S::N \((sp^2)\) hemibond strength is comparable to that of typical 2c/3e S::X bond. The S::N \((sp^2)\) hemibond strength was estimated showing bonding energies around 18-22 kcal/mol. By introducing a methyl group ortho to the H\(_3\)CS– group in MSPPy (3), an even more effective actuating molecule, MMTPPy (11), is proposed. The methyl group functions as a directional block impairing the C–S···N interaction in the neutral state. The MMTPPy (11\(^{+}\)) displays a higher rotational barrier than MSPPy (3\(^{+}\)) along the bridge CC bond of the 2PPy pivot, which also makes it more suitable to function as electro-active materials. The molecular actuators were constructed by equipping the electro-active MMTPPy (11) with rigid beams.

The conformational change of the proposed electroactive biphenyl pivot is based on the formation of an SN hemibond and the first part of the presented material focuses on providing evidence for this. The difference in conformation occurs at different oxidation states, and forms the basis of the proposed actuation mechanism. This is different from atropisomers, where the conformation is maintained by steric effect. The key point of the proposed actuation is that the redox process drives the formation/dissociation of the SN hemibond which in turn moves the equilibrium geometry between two different conformation of the two oxidation states.
The actuation simulations show that the proposed actuators exhibit a relatively large strain response of the order of 88%. More importantly, for the molecular actuators built up with more than one MMTPPy (11) hinge, each unit works independently but in unison in a redox process, and their motions jointly contribute to the actuating behavior of the nano-actuators.

Acknowledgement

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References


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