

S...S Interaction in Pd(II) Complexes of Bis(phosphino)oligothiophene with Various Substituents

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Oligothiophenes have been subjected to a vast number of studies due to their intrinsic optical and electronic properties.¹ Previous studies demonstrate evidently the importance of metal coordination to oligothiophene in order to affect these properties.² Especially, the transition metal containing complexes with conjugated ligands are of significance interest because they allow the metal to influence the overall properties of these complexes which may lead to numerous applications. For instance, Stott *et al.* reported the variation in distance between oligothiophenes depending upon the type of metal used.³ In this regard, the interaction between the metal and conjugated ligand is of fundamental importance. As oligothiophene-based structures illustrate variety of interactions which include van der Waals interactions, π - π stacking, weak hydrogen bonding, and sulfur-sulfur interactions (arising due to the high polarizability of the sulfur atom in thiophene ring). So, it would be intriguing to examine as to how the alteration in terminal ligand environment at

the metal center may result in the instigation of the S...S interactions in complexes having oligothiophene as bridging ligand. Though, the S...S interaction is a weak attractive force in gas and solution, it plays an important role in packing of molecules in crystals. Especially, the S...S interactions are one of the major forces which influence the structures of organic conductors.⁴

This theoretical study of Pd(II) complexes seems to be worth carrying on the basis of following queries. i) What kind of substitution at metal centers incites the S...S interactions in oligothiophenes? ii) Does the nature of the ligand is one of the major factors that influenced the S...S interactions between bridging moieties? iii) Does any relationship between the S...S distance and charge on the S atoms of oligothiophene exist? Through the use of various types of terminal ligands at metal centers in our calculations, we sought to recognize the factors that affected most the structural parameters and stimulated S...S interactions in Pd(II) complexes.

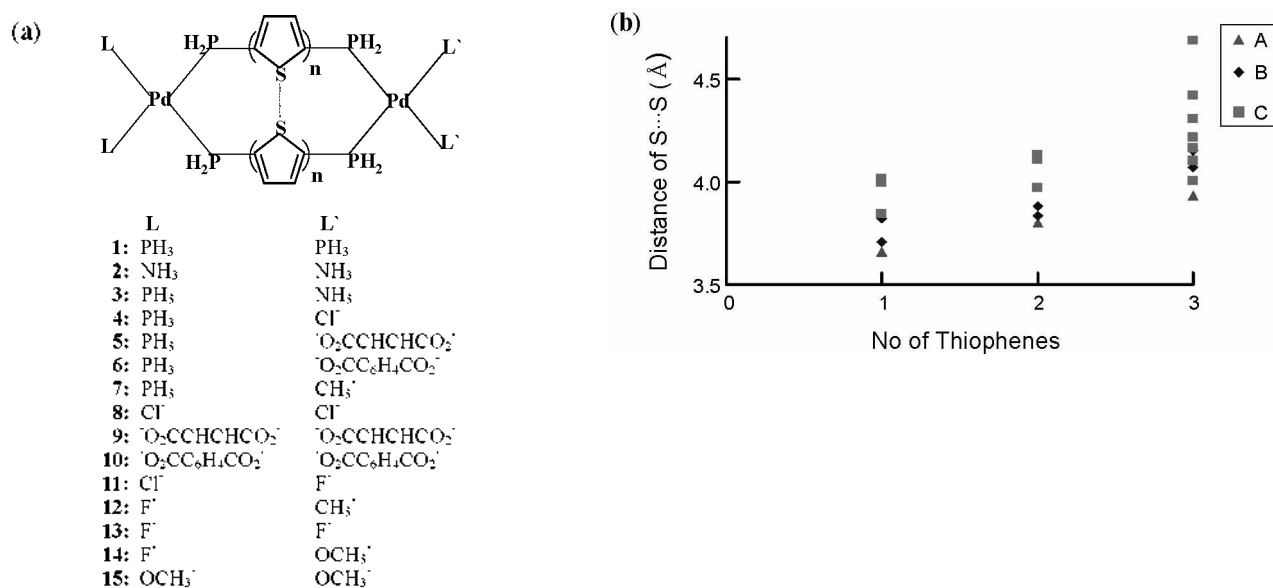


Figure 1. (a) Presentation of the S...S interactions in Pd complex along with terminal and bridging ligands. Here, n = 1 - 3. (b) Variations in the S...S distance of Pd(II) complexes **A** (1-3), **B** (4-7) and **C** (8-15) with respect to the number of thiophenes at the B3LYP/6-31g* (LANL2DZ for Pd) level.

Pd(II) complexes were first optimized with 3-21g* basis set at density functional theory (B3LYP) level using Gaussian 03 package.^{5,6} Finally, the structures were optimized with 6-31g* for C, P, H, O, Cl, F, and N atoms and LANL2DZ for Pd atom. Natural Bond Orbital (NBO) analysis was performed in order to investigate the charge distribution in all complexes. To confirm the existence of stable structures, the harmonic vibrational frequencies of the structures were analyzed at the B3LYP level. Pd(II) complexes having phosphine-substituted monothiophene, bithiophene, and terthiophene bridging ligands are designated as **a**, **b**, and **c**, respectively.

Pd(II) complexes can be classified into three types, which are depended upon the kind of terminal ligands as following: **A** complexes with uncharged terminal ligands, **B** complexes with uncharged and charged terminal ligands, **C** complexes with the charged terminal ligands. The intriguing structural feature of Pd(II) complexes is the distance between sulfur atoms of bridging phosphine-substituted oligothiophenes which may result in strong/weak S...S interactions. The presentation of the S...S interactions in Pd(II) complexes with such a distinctive motif is presented in Figure 1(a). In our optimized structures, the S...S distance lies in the range between 3.662 and 4.688 Å as depicted in the Figure 1(b), whereas twice the van der Waals radius of sulfur atom is 3.70 Å. However, due to broad potential of the van der Waals forces, the distances between sulfur atoms longer than their van der Waals radius could also result in the S...S interactions. So, besides relatively stronger van der Waals S...S interactions, weak van der Waals S...S interactions at longer distance are also present in Pd(II) complexes. The trend in the S...S distance between bridging moieties of Pd(II) complexes

with various terminal ligands is shown in the Figure 1(b). The **A** type complexes exhibit relatively smaller distance (3.662 to 4.071 Å) between sulfur atoms than other complexes. Especially, PH₃ with soft σ -donor and π -acceptor properties of P, augmented π -donation to metal as evident from minimum positive charge (0.20 au) carried by Pd atom adjacent to PH₃. Moreover, the maximum positive charge on S atoms in the **A** type complexes depicted in Figure 2(b), as compared to other complexes also marked enhanced π -donation from bridging oligothiophene ligand to metal center. Thus, the stronger van der Waals S...S interactions (3.662 Å) along with slightly longer one (3.799 to 4.071 Å) than van der Waals radii of S atoms were observed in the **A** type complexes. The S...S van der Waals interactions ranging from 3.85 to 4.29 Å were also reported in experimental studies.^{7,8} While, existence of several long-range van der Waals interactions along with strong S...S interactions which lead to the formation of tubular structures were also reported.⁹

However, in case of the **B** type complexes, the S...S distance varies from 3.705 to 4.152 Å. In these complexes, one of the metal centers coordinates with charged ligands through O, C, Cl, and F atoms and more π -back donation from metal to anionic terminal ligand and bridging oligothiophene occurs. Relatively less positive charge carried by S atoms of the **B** type complexes than the **A** type complexes as shown in Figure 2(a), also indicates this charge transfer to oligothiophene. On the other hand, presence of neutral ligand at the other metal center in the same structure resulted in more π -donation to metal and shaped more symmetric structures. While, in the **C** type complexes, the S...S distances varies from 3.844 to 4.688 Å. The presence of anionic terminal ligands at both metal centers lead to the π -back donation from metal to anionic terminal ligand more vigorously as compared to other complexes. This better π -back donation from metal to anionic terminal ligand is quite evident from the maximum average positive charge (0.54 au) on Pd atoms anchored with anionic terminal ligand. While, relatively high charge values of negatively charged O, C, Cl, and F atoms of anionic ligands also signify this increase in π -back donation from metal to terminal ligands in these complexes. Moreover, minimum positive charge on S atoms of the **C** type complexes as compared to other complexes is also an indication of a better π -back donation in the **C** type complexes. Previous studies have also revealed the electron-withdrawing characteristic of anionic ligand coordinated with Pd metal in oligothiophene containing complex.¹⁰

The molecular orbital variations (HOMO, LUMO) of Pd(II) complexes were also examined meticulously. The gap between HOMO and LUMO levels tends to vary along with the variations in terminal ligands and number of thiophenes as manifested in Figure 2(b). The **B** type complexes exhibit minimum energy gap (0.19 to 1.03 eV) as compared to other complexes. In these complexes, HOMO is localized on metal and the anionic ligand anchored with it and LUMO is composed of the metal center attached with neutral terminal ligands. However, the **A** type complexes display an apparent reduction in HOMO-LUMO gap from 3.20 to 1.59 eV with the increase in number of thiophenes. HOMO and LUMO of these complexes comprise of bridging oligothiophene units and metal atoms, correspondingly. As compared to other complexes, the **C** type complexes with charged terminal ligands hold maximum energy gap varying from 2.72

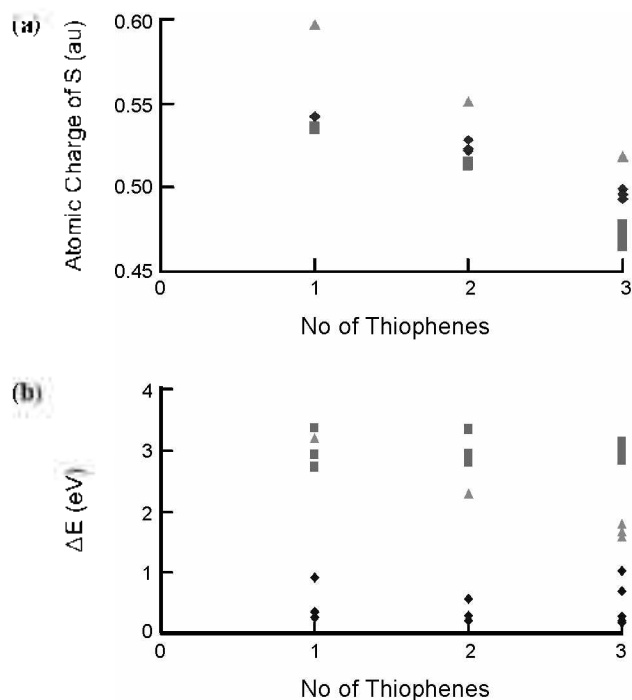


Figure 2. Showing the variations in (a) atomic charge on S atom of thiophene and (b) HOMO-LUMO gap (ΔE) of Pd(II) complexes **A** (▲) (1-3), **B** (◆) (4-7) and **C** (■) (8-15) with respect to the number of thiophenes at the B3LYP/6-31g* (LANL2DZ for Pd) level.

to 3.36 eV and HOMO and LUMO are confined to terminal anionic ligand and metal atoms, respectively.

The geometrical features of thiophene in Pd(II) complexes illustrate slight variation upon change in ligand environment at metal center. The average bond lengths for thiophene rings range from 1.736 to 1.758 Å for C-S bonds, 1.376 to 1.397 Å for C=C bonds, and 1.399 to 1.422 Å for C-C bonds. These bond lengths are comparable to those which are previously reported in other complexes of this type.¹¹ The C-S bond lengths are not equal in oligothiophene due to coordination of two rings with P atom at one α -position. It has also been suggested that enhanced π -back bonding with coordinated thiophene ring would weaken the C-S bond.¹²

In conclusion, this theoretical study reveals various trends in S...S distances among Pd(II) complexes which signify the major influence of the nature of terminal ligands on the strength of van der Waals S...S interactions. Moreover, a strong correlation between the S...S interactions and charge on S atoms of oligothiophene is also revealed. The A type complexes have exhibited minimum S...S distance as compared to other complexes. Consequently, it could be concluded that substitution of uncharged terminal ligand may be more helpful to instigate short sulfur-sulfur interactions in this motif of Pd(II) complexes than charged & uncharged, and charged terminal ligand-containing complexes.

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