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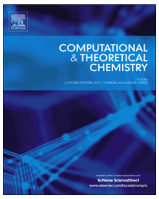

Theoretical evaluation on the reorganization energy of five-ring-fused benzothiophene derivatives

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ABSTRACT

Reorganization energy (λ) is one of the most important parameters regarding the charge transfer in organic semiconductors. In this context, the λ of a series of five-ring-fused benzothiophene derivatives are investigated through density functional theory (DFT). The change of the bond length (Δd), the normal mode (NM) analysis and the highest occupied molecular orbital (HOMO) are employed to shed light on the intricate interplay between reorganization energy and molecular structure (*syn*-, *anti*-isomers and the position of thiophene rings). The results show that within our investigated five-ring-fused benzothiophene derivatives, the λ of *anti*-isomer is larger than its corresponding *syn*-isomer, and the λ tends to increase as the arrangement of thiophene rings tending to concentrating within molecular backbone. From the *syn*- to the *anti*-isomer, the improvement of λ can be mostly ascribed to the benzene ring according to the calculation of Δd. The combined investigation of NM analysis and the distribution of the HOMO shows that the strongly coupled modes are mainly perpendicular to the HOMO distribution. Therefore, the effect of distribution of the HOMO is marked on the hole reorganization energy of these five-ring-fused benzothiophene derivatives. That is, the more similar to *anti*-**S5** the HOMO is, larger the λ; on the contrary, the more similar to **PENT** the HOMO is, smaller the λ.

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1. Introduction

Since first reported in 1986 [1], organic field-effect transistors (OFETs) have attracted great interest for potential applications in low-cost, large-area electronic and optoelectronic devices, including radio frequency identification tags, smart cards, and flexible displays [2]. Pentacene (**PENT**), the most well-known *p*-type organic semiconductor, has achieved a hole mobility of 35 $cm^2\,V^{-1}\,s^{-1}$ at room temperature [3]. However, the oxidative instability and poor solubility of **PENT** under ambient conditions [4] have impeded its further applications. To overcome these defects, several strategies have been applied, such as introducing different substituents and π-conjugated units, changing the position of heteroatom, and so on. In particular, among all the chemical modifications, five-ring-fused benzothiophene derivatives **PENT** analogues, where thiophene rings are used to replace the benzene rings, have aroused widespread concern due to their high mobility and good stability. A number of benzothiophene derivatives, have been designed and synthesized during the last decades [5–11]. For instance, Lee and coworkers [12] synthesized a thiophene-rich heteroacene, dibenzothiopheno[6,5-b:6,5-f]thieno[3,2-b]thiophene (**DBTTT**), the hole mobility obtained in polycrystalline thin-film transistors was up to 19.3 $cm^2\,V^{-1}\,s^{-1}$ by enhancing intermolecular S–S interactions. Minemawari et al. reported another compound, 2 ,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (**C8-BTBT**) [13], yielding thin-film transistors carrier mobility reached **16.4** $cm^2\,V^{-1}\,s^{-1}$ on average and the maximum value was as high as **31.3** $cm^2\,V^{-1}\,s^{-1}$.

Regardless of the exact nature of the transport mechanism, the carrier mobility is highly sensitive to the transfer integral (intermolecular electronic coupling) and the reorganization energy (the local electron–phonon coupling) [14]. Generally, the larger transfer integral and the lower reorganization energy will result in higher charge carrier mobility. Therefore, reorganization energy (λ) is one of the most important parameters governing the charge carrier mobility [15]. So designing new molecule with small λ is a viable method to raise the mobility [16–20]. It has been generally accepted that the value of reorganization energy of five-ring-fused benzothiophene derivatives increases as the number of thiophene ring increases. However, Ren et al. demonstrated that the thiophene-benzene alternate structures are better than acenethiophenes and thienoacenes [21] in terms of lowering λ, which seems

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contrary to the above ‘fact’ in some cases. It is therefore of great interest to discover the effect of thiophene substitution on the reorganization energy of benzothiophene derivative.

In this work, we designed a series of five-ring-fused benzothiophene derivatives from **PENT** to investigate the effect of the number and position of the substituent of thiophene rings on the values of their reorganization energies. All the investigated systems illustrated in Fig. 1 can be named as *anti*/*syn*-*Tn*-*n*, according to the number of thiophene rings (*Tn*) with the prefix (*anti*/*syn*-) denoting neighboring thiophene rings pointing in opposite/same directions and the suffix (-*n*) representing the concentration level of thiophene rings. Herein, we report results of our combined theoretical investigations of the normal mode (NM) analysis, the change of the bond length (Δd), and the characters of the highest occupied molecular orbital (HOMO) to investigate the origin of the variation in λ for five-ring-fused benzothiophene derivatives systematically and seek to establish structure-transport properties relationship. We hope this manuscript would provide some guidance to researchers in designing molecules with small reorganization energy.

2. Methodology

The reorganization energy (λ) describing the strength of the local electron–phonon coupling can be estimated as the sum of the internal and external reorganization energy [22]. However, the intermolecular reorganization energy is much smaller than its intramolecular counterpart in organic solid and it can therefore be neglected [23]. Consequently, we focus here on the intramolecular reorganization energy only. It can be calculated in two ways, namely the adiabatic potential surfaces (AP) and the normal mode analysis (NM).

The intramolecular reorganization energy is caused by the change of the internal nuclear coordinates from the reactant to the product, and the value can be usually evaluated based AP approach [24–26].

$$\lambda_h = \lambda_1 + \lambda_2 = [E^0(M^c) - E^0(M^0)] + [E^c(M^0) - E^c(M^c)]$$

where $E^0(M^0)$ represents the energy of the neutral state with the optimized geometry of neutral molecule, $E^c(M^c)$ represents the energy of the charged states with the optimized charged geometry, $E^0(M^c)$ is the neutral state with the optimized charged geometry and $E^c(M^0)$ is the charged states with the optimized geometry of the neutral molecule.

The λ can be also distributed into the normal modes and given by the following equation [27]:

$$\lambda = \sum \lambda_i = \sum \omega_i S_i = \sum \frac{k}{2} \Delta Q_i^2$$

where S_i represents the Huang–Rhys factor measuring charge–phonon coupling strength, ΔQ_i is the displacement along the normal mode coordinate between the equilibrium positions of charge state and neutral state, ω_i and S_i are the corresponding force constants and vibrational frequencies.

All the quantum chemical calculations were performed with the Gaussian 09 package [28]. The equilibrium structures of the neutral and cation species for five-ring-fused benzothiophene derivatives investigated here were optimized at DFT level with the B3LYP [29] functional and 6-31+G(d) [30] basis set. The NM analysis was made in DUSHIN program [31]. Based on the optimized geometries, the nature of the stationary points was confirmed by means of vibrational frequency analysis at the same level. The hole

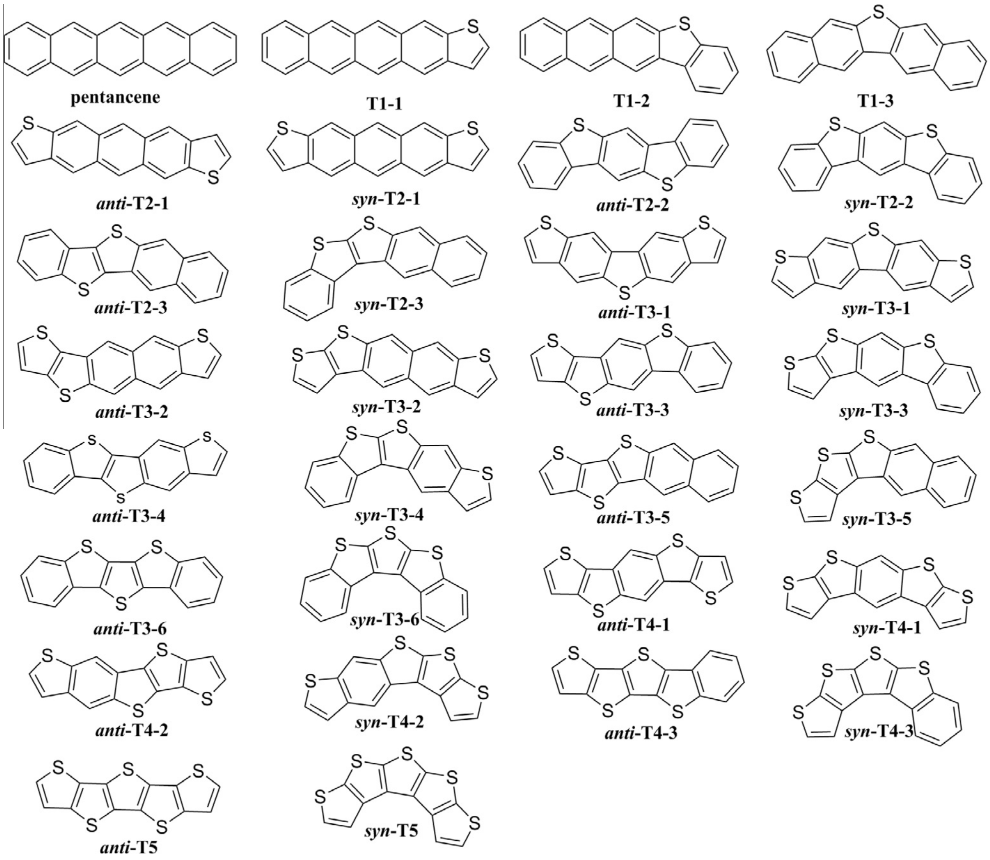

Fig. 1. Molecular structures of the investigated compounds.

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