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# A theoretical study on the isomers of the B5TB heteroacene for improved semiconductor properties in organic electronics

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Abstract: Dibenzodithienothiophene (DBDTT) is a high-performing fused-ring heterocyclic organic semiconductor, with charge-transfer mobilities up to  $1.8 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ , yet attempts to develop this heteroacene with the synthesis of higher homologues such as benzopentathienobenzene (B5TB) have not yielded superior properties ( $0.04 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ ). In this study, we re-worked the structure of B5TB through isomerisation of the terminal benzothiophene rings, which gave a small pool of six isomers. These were theoretically screened to (1) probe their fundamental electronic and optical properties of these new structures, and (2) determine if an isomer of the same chemical formula could impart improved properties over the parent B5TB. In the present study, Density Functional Theory (DFT), Koopmans' Theorem and two electron propagator theories (EPTs) such as the Outer Valence Green's Function (OVGF) and the third-order pole (P3) were applied to calculate properties such as the Frontier Molecular Orbitals (FMOs), the vertical ionization energies and the vertical electron affinities. Marcus Theory was then deployed to determine their hole and electron internal reorganization energies, the transfer integrals at intermolecular separations between  $d = 3.0\text{-}5.0 \text{ \AA}$  via the "splitting-in-dimer" method, and the rates of charge transfer for all structures. The six isomers were found to have a wider HOMO-LUMO gap (*ca.*  $E_g = 3.48\text{-}3.71 \text{ eV}$ ) than that of B5TB ( $2.98 \text{ eV}$ ) and four of which have a greater vertical ionization energy, suggesting excellent air-stability. Two isomers have exceptional hole reorganization energies, as low as  $\lambda_h = 84\text{-}101 \text{ meV}$  and relatively high rates of hole charge transfer ( $0.602 \times 10^{14} \text{ s}^{-1}$ ) at  $d = 4.0 \text{ \AA}$ , which exceed those of B5TB ( $\lambda_h = 240 \text{ meV}$ ,  $K_{CTH} = 0.095 \times 10^{14} \text{ s}^{-1}$ ). Interestingly, all isomers including the parent B5TB showed relatively low electron affinities (*ca.*  $< 1 \text{ eV}$ ), but one has a greater rate of electron charge transfer ( $1.613 \times 10^{14} \text{ s}^{-1}$ ), than that of B5TB ( $1.393 \times 10^{14} \text{ s}^{-1}$ ), suggesting possible ambipolar OTFT applications for these structures. These findings show that the theoretical consideration of structural isomers can significantly improve the physical properties of a given chemical formula and aids the development of the next-generation of organic electronic candidates.

## Introduction

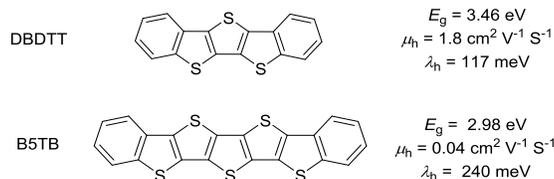
Since the discovery of conducting polyacetylene[1], there has been a surge in research of  $\pi$ -conjugated systems, particularly concerning the development of high-performing materials through the rational design of the molecular structures.  $\pi$ -conjugated systems allow charge to be delocalized over the whole molecule, thereby imparting stability of the unpaired electron towards oxidative or reductive environments. Applications of  $\pi$ -conjugated systems include radio-frequency identification (RFID) tags[2], flexible displays[3], electronic papers[4] and sensors[5]. Yet, limitations still exist in terms of the underlying structure-property relationships for charge transfer.

To date, synthetic iteration has yielded a multitude of fused-ring compounds, of which only a small number[6] have charge carrier mobilities greater than  $1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , such as dibenzodithienothiophene (DBDTT)[6–8] shown in Fig. 1, with selected physical properties. DBDTT has a sufficiently wide HOMO-LUMO gap ( $3.46 \text{ eV}$ ), permitting its application under ambient conditions. The internal hole reorganization energy[9] of DBDTT is  $117 \text{ meV}$ , which is the ideal value for organic

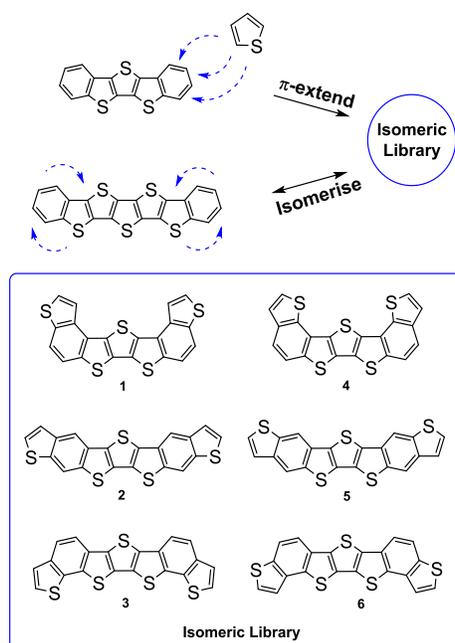
semiconductors (OSCs) [10,11]. It is therefore of great interest to increase the number of fused rings on any high-performing structure to further improve its properties. Benzopentathienobenzene (B5TB)[12,13] is a homologue of DBDTT, which has two more thiophene rings in the core of the molecule, although its HOMO-LUMO gap is lower at 2.98 eV. Disappointingly, B5TB has a far lower charge-transfer mobility at  $0.04 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ , which could be expected from its inferior reorganization energy (240 meV), prompting the present study to determine if isomers of the same chemical formula of B5TB can still yield desirable properties.

Being a seven-membered compound with mixed heterocycles, B5TB can be isomerised to give the same core as DBDTT but with one thiophene unit fused to the terminal edge of each phenyl ring, as illustrated in Scheme 1. As there are three faces and two possible orientations, there are six symmetric isomers of B5TB, or  $\pi$ -extended analogues of DNDTT, and as a result, a number of novel isomeric structures with DBDTT as its core can be created. The heterocyclic unit dithienothiophene (DTT) is a constituent of DNDTT, and is of significant interest to organic electronics in general, as once part of the core, it imparts high thermal stability[14] while the fused phenyl spacers extend the  $\pi$ -conjugation and permit better  $\pi$ - $\pi$  stacking with adjacent molecules. The present study, which looks at how the orientation of the thiophene rings around the DBDTT core imparts the best properties, will aid the future development of structure-based design rules for organic electronic applications.

Identification of suitable candidates can be adequately achieved through the deployment of conventional theoretical approaches, such as the density functional theory (DFT). DFT is now commonplace with experimentalists and is routinely deployed to perform a number of property predictions, such as NMR or fine spectra[15,16]. DFT is the standard choice for the calculation of a range of parameters and the theoretical modelling of complex systems thanks to its approximation of the total electron density, which means that little prior knowledge about the absolute electronic structure is needed. Reliability or ‘chemical accuracy’ of the results is achieved if high quantum mechanical theoretical levels are used, such as with CCSD (T). However, these are computationally expensive and it has been found that less costly theoretical levels, which include basis sets that have diffusion and polarisation functions such as 6-311++G(d,p), still give relatively good correlation to experimental results[17–20]. Such a theoretical level is thus appropriate for an *a priori* DFT study on molecular electronic and optical properties.



**Fig. 1.** High-performing p-type organic semiconductors, DBDTT and B5TB, with their experimentally-derived FMO HOMO-LUMO gaps ( $E_g$ ) from the literature and their internal hole reorganization energies ( $\lambda_h$ ) calculated here.



**Scheme 1.** The process of generating the isomeric library through either a  $\pi$ -extension of DBDTT, or the isomerisation of B5TB, and the structures of the six candidates produced.

Organic semiconducting[6] phenomena are commonplace throughout the literature and yet there are no studies on the re-development of recent  $\pi$ -extended heteroacene candidates such as B5TB for improved properties. The strategy of the present work is threefold: (1) to deploy a theoretical methodology that is well-known in the literature, so that common parameters can be calculated *a priori* to experimental evidence; (2) to calculate parameters that are intrinsic to the structure of the molecule and are not dependent on the electronic device architecture or fabrication procedure; (3) to perform a theoretical screening to identify exemplary structures that are worthy of synthesis and performance testing in future investigations. Such parameters that are intrinsic to the molecular structure and are not device-dependent include the ionization energy ( $IE$ ), the electron affinity ( $EA$ ), the internal hole and electron reorganization energy ( $\lambda_{h,e}$ ), transfer integral ( $t_{h,e}$ ), and rate of charge transfer ( $K_{CT}$ ). Herein, this paper presents the screening of six  $\pi$ -conjugated isomers, based on B5TB, for the identification of improved organic semiconducting candidates for organic electronic material applications.

## Computational methods

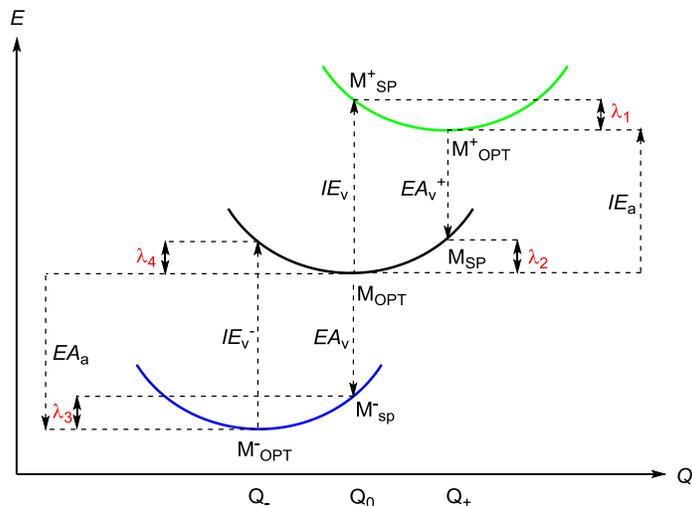
All structures were drawn and visualized in Avogadro[21] (version 1.1.1). All calculations were performed at the B3LYP/6-311++G(d,p) level in Gaussian 09[22] (version D.01). The ground states of the molecular structures were first optimized in Avogadro with the molecular mechanics universal force field (UFF), then optimized with quantum mechanics at the given theoretical level using density functional theory (DFT); all subsequent single-point and vertical calculations were performed in Gaussian 09 (version D.01) from the optimized structures at the same level of theory. All optimized structures were confirmed to be ground state with frequency calculations, *i.e.* no negative frequencies were observed (data available in the ESI†). A number of DFT functionals that are benchmarked against large energetic and structural data sets, such as the Minnesota functionals by Peverati and Truhler [23], which improve on both accuracy and computational cost, are available. The B3LYP functional was used in the present study however, due to its large presence in the literature with regards to describing a wide range of acene and heteroacene OSC structures and their optoelectronic properties with reasonable agreement to experiment [10,24–33].

Although the 6-31G(d) and 6-31+G(d) basis sets have been found to give satisfactory values to experimental observations[25,29,30,34], more-complete basis sets such as of 6-311G to 6-311++G(d,p) are also prevalent throughout the literature[17–20] for higher accuracy where needed. We also deploy the 6-311++G(d,p) basis set, owing to the novel isomer structures of B5TB and the *a priori* charge transfer properties of the isomers, particularly with regards to the dimer separations, as there are no single-crystal experimental observations for comparison with this work.

Different theories were used to evaluate the vertical ionization energies and electron affinities and include DFT (B3LYP), Koopmans' Theorem (KT) and electron propagator theories such as the Outer Valence Green's Function (OVGF) and a variant, the third-order pole (P3). The charge-transfer properties were determined from the semi-classical Marcus Theory, such as the internal reorganization energy, the transfer integral and the rate of charge transfer. Marcus Theory[10] (Equation 1) describes the charge transfer as a self-exchange between a neutral and a charged (radical cation/anion) molecule. One key parameter, the internal reorganization energy[11] ( $\lambda_{h,e}$ ), is intrinsic only to the extent of relaxation and upon which, the electron delocalisation plays a key part. Ideally, internal reorganization energies should be very small, *ca.* 100 meV[35].

$$k_{ct} = \left(\frac{t^2}{\hbar}\right) \left(\frac{\pi}{\lambda k_B T}\right)^{1/2} e^{\frac{-\lambda}{4k_B T}} \quad (1)$$

A vertically excited state is the immediate nature of a molecule which has gained or lost an electron and an adiabatic state is where the vertical state has relaxed to a minima on its potential energy surface. The energy processes of electron exchange, excitation and relaxation are illustrated in Fig. 2. The internal hole reorganization energy ( $\lambda_h$ ) is comprised of two relaxation terms, the energy of the cationic ( $\lambda_1$ ) and neutral ( $\lambda_2$ ) surfaces, as defined in Equation 2.



**Fig. 2.** The ionization energy ( $IE$ ) and electron affinity ( $EA$ ) pathways between the anion (blue), neutral (black) and cation (green) potential energy surfaces for the calculation of the hole (electron) reorganization energy  $\lambda_h$  ( $\lambda_e$ ).

$$\lambda_h = \lambda_1 + \lambda_2 \quad (2)$$

The cationic reorganization energy  $\lambda_1$  is determined from the difference between the vertical and adiabatic ionization energies calculated *via* the vertical, single-point geometry of the cation ( $M^+_{SP}$ ) and the optimized cation structure ( $M^+_{OPT}$ ), (Equation 3).

$$\lambda_1 = E(M^+_{SP}) - E(M^+_{OPT}) \quad (3)$$

Addition of an electron to the minimised cationic structure returns the molecule back to its neutral geometry and is performed with a vertical electron affinity of the cation,  $EA_v^+$ ; the difference between this state and the minimum of the neutral molecule is  $\lambda_2$  (Equation 4).

$$\lambda_2 = E(M_{SP}) - E(M_{OPT}) \quad (4)$$

Similarly, the internal electron reorganization energy  $\lambda_e$ , is calculated according to Equation 5, which is the difference of the constituent relaxations between the anionic ( $\lambda_3$ ) and the neutral surfaces ( $\lambda_4$ ), from Equations 6 and 7 respectively.

$$\lambda_e = \lambda_3 + \lambda_4 \quad (5)$$

$$\lambda_3 = E(M^-_{SP}) - E(M^-_{OPT}) \quad (6)$$

$$\lambda_4 = E(M^-_{OPT}) - E(M^-_{SP}) \quad (7)$$

The transfer integral  $t_h$  is another important component in Marcus Theory and the hole integral can be estimated from the “splitting-in-dimer” method[19,24,25,28] (Equation 8), comprising of two cofacial molecules separated by a distance  $d$  (Å) and determined from calculating half the energy difference between the HOMO and HOMO-1 levels of the dimer. The electron transfer integral ( $t_e$ ) is determined from the half difference between the energies of the LUMO+1 and LUMO states (Equation 9).

A range of dimer separations are appropriate to determine the extent of the electronic coupling interaction. Although a separation between  $d = 3.3$ - $3.8$  Å was found to be suitable for OSCs[20,25,28], it

is reasonable to assume that not all of the other isomers in this study, some being non-planar, will have an identical packing arrangement, and thus integrals were calculated with 0.5 Å between them, starting at 3.0 Å and ending at 5.0 Å inclusive; this 2 Å wide intermolecular range brackets known single-crystal packing separations for fused-ring OSCs[36–39]. Substituting values for  $\lambda$  and  $t$  into Equation 1, enables the rates of hole and electron charge transfer ( $K_{CT,h,e}$ ) to be determined at any given separation  $d$ .

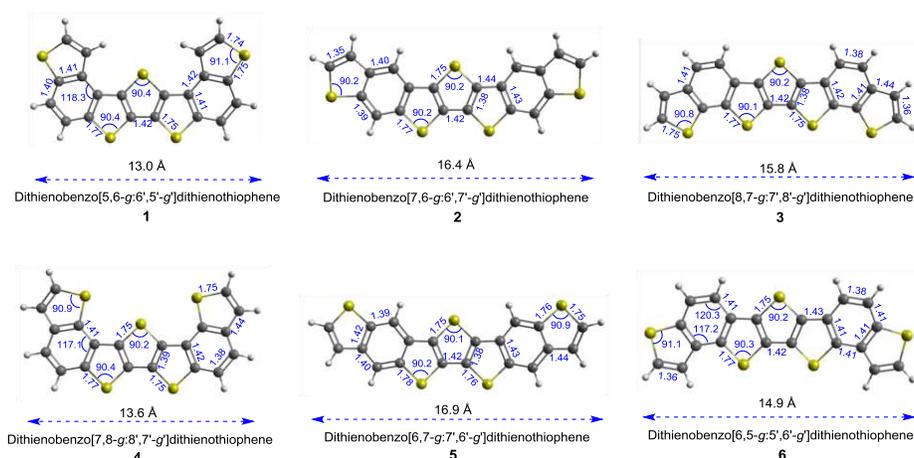
Limitations of Marcus theory include the absence of configurational entropy, electronic coupling over a wide temperature range and nuclear tunneling, which have been incorporated, inter alia, with the Marcus-Levich-Jortner equation[40,41] and that of McConnell's[42]. Although other charge transfer theories are available[43], Marcus theory is routinely revised to include polaronic effects for accurate solid-state predictions[33] and non-equilibrium thermodynamics[44], but the more simplified approach which is still used widely in the literature[25,45,46] and deployed in the present study, is suitable for *a priori* investigations on novel compounds.

$$t_h = \frac{1}{2}(\Phi_H - \Phi_{H-1}) \quad (8)$$

$$t_e = \frac{1}{2}(\Phi_{L+1} - \Phi_L) \quad (9)$$

## Results and Discussion

The structures of the six DTBDTT isomers from the  $\pi$ -expansion or isomerisation are illustrated in Fig. 3, with selected geometric parameters. They consist of the central DBDTT core with the thiophene heterocycles fused to the terminal phenyl edges in various arrangements, which in turn generates varying molecular shapes and sizes, with lengths between 13 and 17 Å. The isomers **1-3** have the thiophene *anti* to the central thiophene in the DTT core, with those of **4-6** being *syn*. The most curved and smallest structures are **1** and **4**, with only 13.0 and 13.6 Å in length; the most linear are **2** and **5**, with lengths up to 16.9 Å, while **3** and **6** are phenacene-like and less than 16 Å.



**Fig. 3.** Structures of the isomeric pool of symmetric fused-ring systems **1-6** based on the parent B5TB, with selected geometric parameters.

Frontier molecular orbital properties are of interest in organic electronics, as air-stability and compatibility between the ground state and the work function of the metal electrodes in organic devices are prominent issues. Table 1 shows the deep HOMO energy levels of isomers **1** and **2** are of almost identical energy *ca.* -5.62 eV, with isomer **3** being exceptionally close at -5.60 eV; all isomers have remarkably similar HOMO energies to the experimentally determined value of -5.64 eV for B5TB. High HOMO energies are a known stability issue for acenes such as pentacene, but isomers such as picene have deeper HOMO levels, and it was found that the HOMO level needs to be 5.2 eV below the vacuum level for p-type materials[47]. Here, the isomeric pool of these heteroacene candidates show similar deep energy levels to that of picene and thus strong suitability for air-stable organic electronic applications. Isomers **1-3** and **5** have low LUMO energy levels (-2.03 to -1.91 eV), whereas those of **4** and **6** are slightly higher between -1.86 and -1.72 eV respectively. Their resulting HOMO-LUMO energy gaps are relatively larger than B5TB; knowing that B5TB is an air-stable structure, the isomers **1-6** are thus expected to have excellent air-stability.

The HOMO orbitals form a ladder-like array across the breadth of the molecules, exemplified with B5TB. Isomers **1**, **2** and **4** are interesting with regards to the lack of orbital density on particular carbon atoms of the thiophene unit, noticeably at the connecting and fused carbon atoms with the phenyl ring for **1** and **4**, but on the terminal carbon of the thiophene with isomer **2**. This occurs evidently from the

greater overlap with those of the phenyl ring for these isomers, where the molecular orbitals share three fused atoms between both the thiophene and the phenyl ring; isomer **6** is a very close contender to this phenomena due to little orbital density on the terminal thiophene carbon.

In the LUMO state, the orbitals of isomers **1** and **4** show the same phenomena, with isomer **2** being the exception. Those which have orbitals in the same phase across the carbon atoms in a linear array, have a relatively stabilised LUMO energy, such as isomers **1** (2.03 eV) and **5** (-2.08 eV), while those of isomers **2** and **6** have a discontinuity at the peripheral thiophene carbons. The central orbitals around the DTT unit remain largely unchanged in both the HOMO and LUMO states.

**Table 1**

Frontier molecular orbitals (FMOs) of all isomers and the parent B5TB with their energies in electron volts (eV).

Isomer	$\psi_H$	$\epsilon_H$	$\psi_L$	$\epsilon_L$	$E_g$
<b>1</b>		-5.62		-2.03	3.59
<b>2</b>		-5.62		-1.91	3.71
<b>3</b>		-5.60		-1.95	3.65
<b>4</b>		-5.66		-1.86	3.80
<b>5</b>		-5.56		-2.08	3.48
<b>6</b>		-5.67		-1.72	3.95
<b>B5TB</b>		-5.58		-2.08	3.50

The vertical ionization energies ( $I_E$ ) were calculated for isomers **1-6**, using DFT and EPT methods and presented in Table 2, along with the parent isomer B5TB for comparison. The ionization energy for p-type organic semiconductors should be relatively large, *ca.* 5.0 eV such as with pentacene[6] or 5.81 eV with fluorinated acenes[48]. All isomers show exceptional ionizations, as high as 7.25 eV with DFT of isomer **6**, followed closely by that of **2** with 7.07 eV. Moreover, the EPT ionization energies are also high, and have relatively similar energies between those of OVGf and B3LYP; exceptions being isomers **2** and **6**. Previously, it was found that P3 give the most accurate vertical ionizations for acenes[31], and show a remarkable similarity between the energies of all the heteroacene **1-6** and parent isomer B5TB. Interestingly, **1**, **3**, **4** and **6** have ionizations greater than B5TB, with **2** and **5** being relatively lower.

The electron affinities calculated with DFT, KT and EPT functions are also presented in Table 2. The lowest value with B3LYP was found with isomer **6** (0.53 eV) while the greatest was with isomer **5** (0.92 eV); KT gave relatively larger values, up to 1.22 eV with **2**. Some of the lowest electron affinities were observed with the OVGf and P3 functions, specifically with isomer **5**, although B5TB had the lowest out of both of these functions. The OVGf and P3 functions give relatively similar electron affinities, regardless of the molecular structure, while the B3LYP and KT functions differ by up to 0.52 eV with isomer **6**. It is

known for n-types that the lower and upper limits[10,11] for electron affinity is 3.0 and 4.0 eV respectively, indicating that the isomers and the parent B5TB are not suitable for n-type devices.

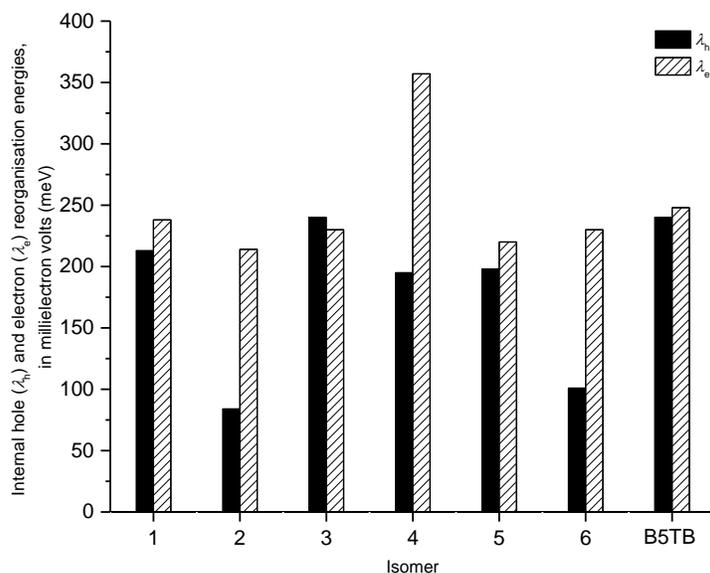
**Table 2**

Calculated vertical ionization energies ( $IE_V$ ) and vertical electron affinities ( $EA_V$ ) in electron volts (eV) of isomers **1-6** and B5TB for comparison using DFT (B3LYP), KT and EPT (OVGF, P3); their pole strengths are in parenthesis.

Isomer	$IE_V$				$EA_V$			
	B3LYP	KT	OVGF	P3	B3LYP	KT	OVGF	P3
<b>1</b>	6.85	7.25	6.81 (0.88)	7.43 (0.87)	0.83	0.97	0.67 (0.98)	0.61 (0.98)
<b>2</b>	7.07	7.30	6.77 (0.88)	7.38 (0.86)	0.72	1.22	0.21 (0.90)	0.13 (0.89)
<b>3</b>	6.82	7.19	6.73 (0.88)	7.41 (0.86)	0.77	1.09	0.14 (0.90)	0.097 (0.88)
<b>4</b>	6.89	7.28	6.85 (0.88)	7.43 (0.87)	0.54	1.00	0.705 (0.98)	0.65 (0.98)
<b>5</b>	6.75	7.17	6.76 (0.88)	7.35 (0.86)	0.92	0.98	0.038 (0.89)	0.082 (0.88)
<b>6</b>	7.25	7.33	6.82 (0.88)	7.45 (0.86)	0.53	1.05	0.73 (0.98)	0.68 (0.98)
<b>B5TB</b>	6.79	7.15	6.72 (0.88)	7.39 (0.86)	0.90	0.94	0.018 (0.90)	0.029 (0.88)

Now the hole charge transfer properties including the internal reorganization energy ( $\lambda_h$ ), transfer integrals ( $t_h$ ) at dimer separations between  $d = 3.0-5.0$  Å inclusive, and rates of charge transfer ( $K_{CTH}$ ) were calculated for isomers **1-6** and those for the parent isomer B5TB for comparison; these are presented in Table 3 and 4. Although the origin of small reorganization energies are not known, Troisi reports[49] that the most significant relaxation contributions arise from C-C vibrational modes, *ca.* 800-1200  $\text{cm}^{-1}$ , while Zhu *et al.* finds 1500  $\text{cm}^{-1}$  [50]. The internal hole reorganization energy for isomer **2** (84 meV) is relatively lower than those of tetracene (114 meV) and rubrene[32] (159 meV) and significantly lower than the calculated value for B5TB (240 meV). Isomer **6** also has an exceptional hole reorganization energy (101 meV), while **4** and **5** are modest with 195 meV and 198 meV respectively. Hole reorganization energies for five-membered thiophene-based analogues of pentacene[50] range between 91-299 meV, depending on the position and the orientation of the thiophene ring, suggesting the seven-membered isomers in this study are suitable for organic p-type semiconductors.

The electron reorganization energies were calculated for all isomers (Table 3 and 4, illustrated in Fig. 5), and although the structures had values between 214-357 meV, only isomer **4** (357 meV) exceeded that of B5TB (248 meV), suggesting the isomers in general had slightly improved n-type properties. Moreover, the electron reorganization energies of isomers **2** and **5** are not far from with values of nitrogen substituted acenes[10]. An overall comparison between the hole and electron reorganization energies for all isomers is shown in Fig. 4. Isomers **1**, **3** and **5** have similar hole and electron energies to B5TB, while the hole reorganization energies of isomers **2** and **6** are as much as half that of their electron reorganization.



**Fig. 4.** Internal hole ( $\lambda_h$ ) and electron ( $\lambda_e$ ) reorganization energies in millielectron volts (meV) for each isomer.

In general, the hole transfer integrals ( $t_h$ ) show a maxima between 3.5-4.0 Å, suggesting that the intermolecular distances of these structures in the solid state may occur within this range; as observed for similar fused ring heteroacenes[36–39]. B5TB has the largest integral at  $d = 3.0$  Å (113 meV), but relatively similar to isomers **3** (137 meV), **5** (135) and **6** (138) at  $d = 4.0$  Å. The largest hole transfer integral is 197 meV and reached with B5TB at  $d = 3.5$  Å, which is also the best separation for the integrals of isomers **1** (163 meV) and **3** (165 meV). This significantly changes at  $d = 4.0$  Å, where B5TB becomes the second lowest (134 meV) and isomers **4-6** reaching their maxima at this separation (135-156 meV). Interestingly, isomers **1** and **3** still have greater integrals than B5TB for  $d = 4.0$  Å at 152 meV and 156 meV respectively. The hole integral collectively falls at 4.5 Å for all isomers and lower still at 5.0 Å.

Similarly, the electron transfer integral is greatest with B5TB at  $d = 3.0$  Å (538 meV), but all isomers show a decreasing trend from 3.0 to 5.0 Å. Excluding **6**, the electron integrals at  $d = 3.5$  Å are closer than the hole integrals and average at 353 meV. The electron integral energies at  $d = 4.0$  Å are relatively similar, ranging between 169 meV and 178 meV, and are closer together still at 4.5-5.0 Å, with some being identical, such as with isomers **6** and B5TB (86 meV at  $d = 4.5$  Å and 44 meV at  $d = 5.0$  Å). Comparable transfer integrals for both hole and electron are observed with small[33] and extended acenes[51], circumacenes [25]and acene diimides[43].

The rates of both hole and electron charge transfer show a similar pattern to the integrals, and the largest rate was found for isomer **6** at  $d = 4.0$  Å ( $0.602 \times 10^{14} \text{ s}^{-1}$ ), followed closely by **2** ( $0.395 \times 10^{14} \text{ s}^{-1}$ ). This is due to the hole reorganization energies of isomers **2** and **6** being exceptional and shows the importance of the reorganization term with regards to charge transfer. Moreover, the order of magnitude for all isomers including the parent isomer B5TB, is of the same order as the previously studied pentacene's isomers[31,47] ( $\times 10^{14} \text{ s}^{-1}$ ), suggesting these fused-ring heteroacenes have significant potential as high-performing p-type organic semiconductors.

The largest rate of electron charge transfer was observed with isomer **5** at  $d = 3.0 \text{ \AA}$  ( $1.613 \times 10^{14} \text{ s}^{-1}$ ), closely beating B5TB ( $1.393 \times 10^{14} \text{ s}^{-1}$ ) and followed with isomer **3** ( $1.193 \times 10^{14} \text{ s}^{-1}$ ). Their order of magnitude ( $\times 10^{14} \text{ s}^{-1}$ ) is the same as the hole charge transfer rates as determined above, which suggests these structures have potential as ambipolar semiconductors. Fig. 5 shows both the transfer integrals and the rates of charge transfer versus  $d$  for all isomers.

**Table 3**

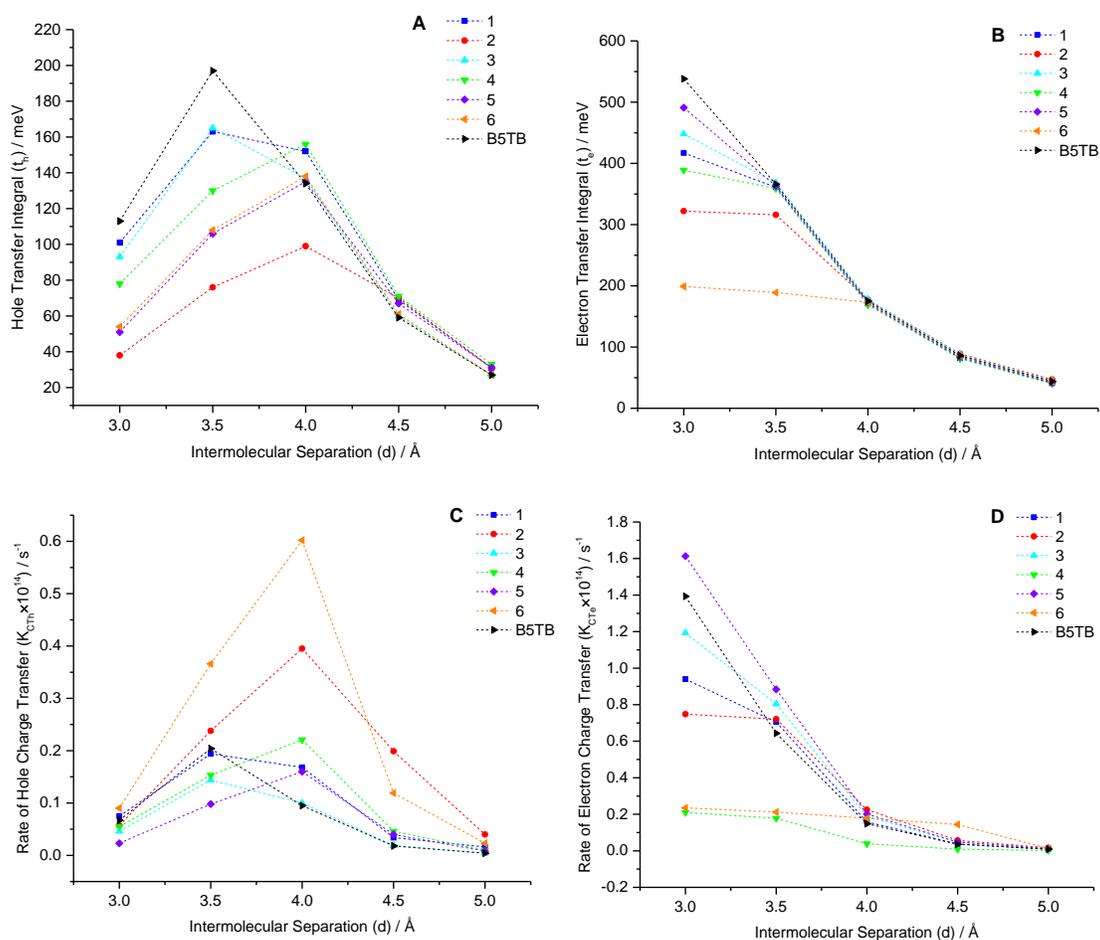
Hole reorganization energy ( $\lambda_h / \text{meV}$ ) for each isomer and the hole transfer integral ( $t_h / \text{meV}$ ) with the rate of hole charge Transfer ( $K_{CTh} \times 10^{14} / \text{s}^{-1}$ ) for each intermolecular separation of  $d = 3.0, 3.5$  and  $4.0 \text{ \AA}$ .

Isomer	$\lambda_h$	$d = 3.0 \text{ \AA}$		$d = 3.5 \text{ \AA}$		$d = 4.0 \text{ \AA}$		$d = 4.5 \text{ \AA}$		$d = 5.0 \text{ \AA}$	
		$t_h$	$K_{CTh}$								
<b>1</b>	213	101	0.075	163	0.194	152	0.168	69	0.034	31	0.016
<b>2</b>	84	38	0.057	76	0.238	99	0.395	70	0.199	31	0.040
<b>3</b>	240	93	0.046	165	0.144	137	0.100	60	0.019	27	0.004
<b>4</b>	195	78	0.055	130	0.153	156	0.221	71	0.046	33	0.010
<b>5</b>	198	51	0.023	106	0.098	135	0.160	67	0.040	31	0.008
<b>6</b>	101	54	0.090	108	0.366	138	0.602	61	0.119	27	0.023
<b>B5TB</b>	240	113	0.067	197	0.204	134	0.095	59	0.018	27	0.004

**Table 4**

Electron reorganization energy ( $\lambda_e / \text{meV}$ ) for each isomer and the electron transfer integral ( $t_e / \text{meV}$ ) with the rate of electron charge transfer ( $K_{CTe} \times 10^{14} / \text{s}^{-1}$ ) for each Intermolecular separation of  $d = 3.0, 3.5$  and  $4.0 \text{ \AA}$ .

Isomer	$\lambda_e$	$d = 3.0 \text{ \AA}$		$d = 3.5 \text{ \AA}$		$d = 4.0 \text{ \AA}$		$d = 4.5 \text{ \AA}$		$d = 5.0 \text{ \AA}$	
		$t_e$	$K_{CTe}$								
<b>1</b>	238	417	0.940	361	0.705	171	0.158	82	0.037	41	0.009
<b>2</b>	214	322	0.748	316	0.721	177	0.225	89	0.057	47	0.016
<b>3</b>	230	448	1.193	368	0.804	178	0.189	88	0.046	45	0.012
<b>4</b>	357	389	0.210	359	0.178	169	0.039	81	0.009	40	0.002
<b>5</b>	220	491	1.613	363	0.884	173	0.201	84	0.048	42	0.012
<b>6</b>	230	199	0.235	189	0.212	173	0.178	86	0.044	44	0.012
<b>B5TB</b>	248	538	1.393	366	0.643	175	0.148	86	0.036	44	0.009



**Fig. 5.** Transfer integrals (A,B) and rates of charge transfer (C,D) for hole and electron, respectively.

## Conclusion

A small isomeric pool of extended fused-ring benzothiophene structures based on the B5TB heteroacene were theoretically screened with DFT and EPT functions. The regioposition of the end-capping thiophene is shown to have a strong effect on both the electronic and the optical properties of the molecule. It was found that all isomers have a deep HOMO level and a wider HOMO-LUMO gap ( $E_g$ ) than the parent B5TB, suggesting air-stability for these isomers. Their vertical ionization energies were found to be high and relatively similar with the third-order pole (P3), with most isomers having slightly larger values than B5TB. Unfortunately, all structures including B5TB showed low electron affinities that lie outside of the 3-4 eV threshold, and are thus not suitable for n-type semiconductors.

All isomers show a greater rate of both hole and electron charge transfer than B5TB at the intermolecular spacing  $d = 3.5\text{-}4.0$  Å. The order of magnitude for both hole and electron rates of charge transfer suggests these isomers have significant potential as ambipolar organic semiconductors. A common practice is to fluorinate the terminal C-H positions which could raise the electron affinities and ensure suitable n-type properties; these studies are currently underway in our laboratories. These findings highlight the merit of a theoretical approach to screen target parent candidates and their possible isomers

for the prediction of their fundamental charge transfer properties, before experimental investigations and thus reduce resources. Overall, a number of isomers were found to have superior properties to the parent B5TB and are thus promising candidates for organic semiconducting materials.

### Key Words

Organic semiconductors; charge transfer; computational materials chemistry; DFT

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