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"Abnormal" bromination reaction selectivity of 5-diarylamino-2-methylbenzo[b]thiophene caused by a "non-planar" conjugated model: Synthesis and theoretical calculation

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HIGHLIGHTS

- The molecular simulation of TPA-based compounds having a benzo[b]thiopheng unit was performed.
- "Abnormal" bromination selectivity of the compounds was predicted.
- Four new compounds were synthesized.
- One of the "abnormal" products was characterized by single-crystal X-ray diffraction.
- The primary cause for the "abnormal" selectivity was explained by a "non-planar" conjugated model.

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ABSTRACT

5-Diarylamino-2-methylbenzo[b]thiophene was a new kind of triphenylamine-based charge-transporting material. For further modification of the compounds, bromination selectivity was studied through experiments and molecular simulation using Gaussian 09 program under B3LYP/6-311G (d, p) aided by Gaussian View 05 and Multiwfn Program. The results showed that bromination of 5-diarylamino-2-methyl-benzo[b]thiophene would occurred at an "abnormal" positions (4- and/or 4′-position) rather than at the "normal" position (3-position), which was different from those benzo[b]thiophene derivatives with simple 5-substitutes reported in literatures. The "abnormal" selectivity resulted from a special electron structure in which there was an "interfinger-like" frontier orbital or a special "non-planar" conjugated model. Electrons would be donated to the *o*- and *p*-positions of linked aromatic rings by this manner of electron delocalization, so that TPA unit rather than thiophene ring became the main factor in the selectivity, and reaction active energy at 4-position was lowest. The results were confirmed by the synthesis of three 4-Br and/or 4′-Br derivatives, compound **4**, **5** and **6**. Single crystal X-ray diffraction of compound **6** gave conclusive evidence on the abnormal selectivity.

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1. Introduction

Triphenyamine (TPA) is an important molecule which has a basic structure of charge-transport function. The compounds having TPA unit are a kind of useful organic semiconductor materials in the field of electro-luminescence [1]. However, TPA itself subjected to greater limitations in actual applications for its low melt point, no easy to form a film, easy to crystallize and be oxidized. The molecules modified with TPA unit could also be used as organic dye [2]. A lot of research had focused on the modification of TPA [3,4]. The compounds having benzo[b]thiophene unit were often used in the preparation of photochromic materials [5–7] and pharmaceutical intermediates [8].

When TPA and benzo[b]thiophene units were combined in one molecule, a new series of functional molecules were expected to be obtained. 5-Diarylamino-2-methylbenzo[b]thiophene had been prepared by introducing a diarylamino into the 5-position of 2-methyl-benzo[b]thiophene in our previous works. According to the experiments in literatures [9–18], 5-substituted-2-methylbenzo[b]thiophene derivatives (Fig. 1a) generally had a fixed active position named as "normal" position (3-position of thiophene ring), whatever the 5-substituent was electron-accepting or electron-donating group (Table 1) [9–18]. The relatively higher activity of electrophilic substitution of thiophene ring may be the reasonable explanation for the selectivity. In this paper, the bromination of

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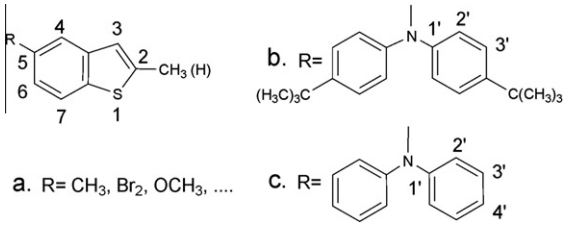


Fig. 1. 5-Substituted-2-methylbenzo[b]thiophene derivatives.

Table 1
Electrophilic substitution reactions of 5-substituted-2-methylbenzo[b]thiophene reported in literatures.

–R	Bromination	Acetylation	Product (yield)
–H	√[13, 14, 15]	√[9]	3-Br (63–95%), 3-acetyl (30–40%)
$-CH_3$	√[13]	√[10]	3-Br([b]), 3-acetyl (77%)
$-OCH_3$	√[16]	[a]	3-Br(68%)
–Br	√[12]	√[11]	3-Br([b]), 3-acetyl (93%)
$-COOCH_3$	√[17]	[a]	3-Br([b])
$-NH_2$·HCl	√[18]	[a]	3-Br([b])
$-NO_2$	√[19]	[a]	3-Br (64%)

[a] Not reported.
[b] Not given in abstract and original text not available for us.

5-diarylamino-2-methylbenzo[b]thiophene was investigated in order to make additional modification of novel compounds.

As it was known to us, amino or substituted amino was usually strong active group for the electrophilic substitution of aromatic ring. When diarylamino was attached to the 5-position of 2-methylbenzo[b]thiophene (Fig. 1b and c), a question would be put forward: whether the reaction still had the "normal" position selectivity as usual. Because there were two typical structure units (TPA and benzo[b]thiophene units) in the molecule, it seemed much more indecisive to predict the selectivity according to some experiential laws in organic chemistry. Therefore, bromination might form various products. Which was the main product in the synthesis and whether it had the practical value? By this token, it should be worth understanding the structure–activity relationships of this molecular system both for theoretical research and design of new materials.

Semi-empirical method, such as resonance theory, and theoretical calculations (molecular simulation) are the two ways to predict the selectivity of electrophilic substitution. For simple aromatic systems, resonance theory can give reasonable prediction according to the stability of resonance hybrid in most cases. Along with the development of computational chemistry, theoretical calculation based on existing basis sets instead of experiments in lab is expected to deduce reliable description of complex systems. The researches on Fukui function, especially condensed Fukui function (CFF) being used as reactive parameters, have attracted widespread attentions [19]. CFF had been successfully applied to predict the active sites of mono-substituted and di-substituted benzene in electrophilic substitution of aromatic compounds, which is very consistent with experiments and organic chemistry concepts [20–22].

We performed the molecular simulation of 5-substituted-2-methyl-benzo[b]thiophene using Gaussian 09 Program [23] aided by Gaussian View 05 Software and Multiwfn Program [24]. Some related compounds had been synthesized (Fig. 1b and c) and were characterized by means of ^{1}H NMR, ^{13}C NMR and HRESI-MS. One crystal structure was determined for further confirmation.

2. Results and discussion

2.1. Molecular simulation

Theoretical calculations were performed by a fully first-principles scheme combining DFT with B3LYP/6-311G (d, p) method [25]. Geometric optimizations and electronic structures are calculated using linear combinations of atomic orbitals as basis set. Because the bromination of the title compounds occurred in the aromatic ring of benzo[b]thiophene, the reaction belonged to electrophilic substitution, and the distribution of electrons involved in the reaction process would be the key to the question.

Generally, the atomic charge at any possible reactive site was usually calculated to explain reaction selectivity of electrophilic substitution. Mulliken atomic charge and NPA (natural population analysis) charge are the two primary forms of atomic charge, which results from two different theories and models. According to the theory of molecular simulation, NPA atomic charge is more reasonable than Mulliken atomic charge. After geometric optimizations by Gaussian Program under proper level of calculation, NPA charge could be calculated. The larger negative value would indicate greater activity in electrophilic substitution. Conclusions were relatively consistent with experiments and some experiential laws based on electronic effects of substitutes for some simple systems, such as mono-substituted benzene or heterocyclic compounds [25]. But, it was not always the case, especially for some rather complex systems.

In order to determine if the calculation method was appropriate for 5-substituted-2-methylbenzo[b]thiophene system, some compounds with simple substitutes were firstly selected for calculation. It was found that, if atomic charge was only taken for the prediction of reaction selectivity, the conclusions were not satisfactorily consistent with reported experiments, and sometimes contradictory. Some data resulted from molecular simulation was not listed in this paper. A reasonable explanation may be that

Table 2
Electron distribution and the relatively more active sites.

–R	$\Delta\rho_i$ C3/C4/C6/C7/C2′/C3′/C4′	Most active sites based on isosurface (f^-)	The sites[a] related to HOMO
$-CH_3$	−**0.32682**/−0.30156/−0.19631/−0.22757	3-	3-
$-OCH_3$	−0.25060/−**0.32376**/0.143025/−0.209114	4-	3-
–Br	−0.12879/−**0.12983**/−0.03371/−0.09741	(4-)	3-
–N, N-diphenylamino	−0.13735/−**0.17219**/−0.13796/−0.10477/−**0.17615**/−0.08003/−**0.20716**	4′-, (2′-)[b], 4-,	4-, 4′-, (2′-, 6-)[b]
–N, N-bis(4-tert-butylphenyl) amino	−0.13497/−**0.17108**/−0.14090/0.08192/−**0.17125**/−0.08552/–/	4-, (2′-)[b]	4-, (4′-, 2′, 6-)[b]

[a] Higher energy occupied MOs (related to more reactive site).
[b] No product from experiment.

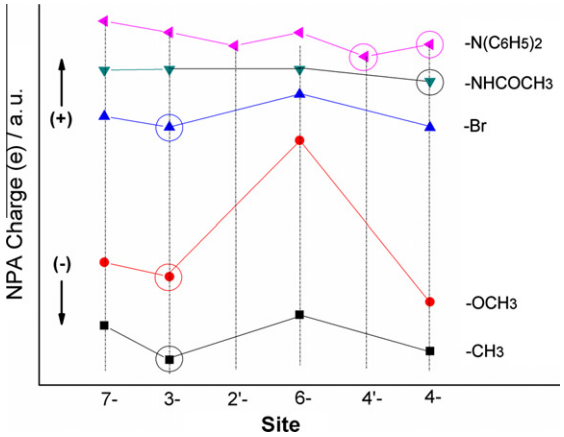


Fig. 2. $\Delta\rho_i$ based on NPA of 5-substituted-2-methylbenzo[b]thiophene derivatives (in atom unit). The circle marks are the more active sites according to experiments.

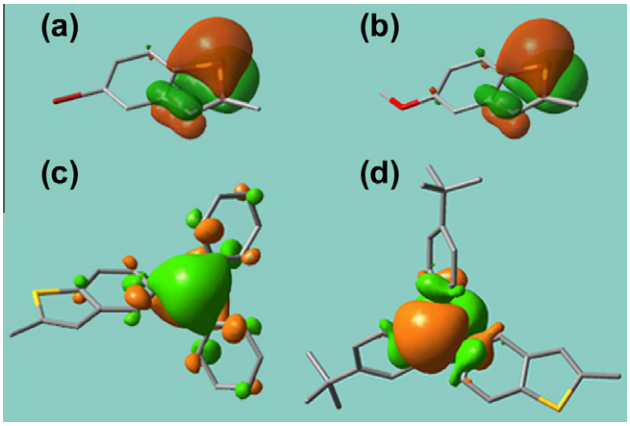


Fig. 3. Electron distribution of HOMO's: (a) HOMO (orbital No. 56) of 5-Br derivative (isovalue = 0.015). (b) HOMO (orbital No. 47) of 5-OCH_3 derivative (isovalue = 0.020). (c) HOMO (orbital No. 83) of compound **2** (isovalue = 0.010). (d) HOMO (orbital No. 115) of compound **3** (isovalue = 0.005).

NPA atomic charge of electrically neutral molecule (N electrons system) could not be perfectly reasonable to describe the situation when substrate was attacked by electrophillic reagents. The key active intermediate in bromination was σ-complex that was more properly represented by N−1 electrons system. In this situation, the calculation using Fukui Function ($f^- = \rho(N) - \rho(N-1) = \Delta\rho$) would be a better choice under the same level for the analysis of electron density difference ($\Delta\rho$) [25]. f^-, $\rho(N)$ and $\rho(N-1)$ are Density Functions in three dimension. The $\rho(N)$ and $\rho(N-1)$ presents the Density Function of the systems with N electrons and N−1 electrons, respectively. The reaction selectivity could be showed in two ways as follows.

According to NBO (natural bond orbital) Theory [25], when the Fukui Function converges to a single atom in the molecule, the value of f^- became the value of f_i^- ($f_i^- = q_i(N) - q_i(N-1)$), which is equals to the difference ($\Delta\rho_i$) of NPA atomic charge with N and N−1 electrons systems. The $\Delta\rho_i$ calculated based on NPA atom charge were shown in Table 2 and Fig. 2. The calculation results revealed that 4- (or 4′) and 3-positions were really the competitive sites in any way, and 4- (or 4′-) position should be more active site than 3-, except for 5-CH_3 system. It seemed that the conclusion is not exactly consistent with experiments (as shown in Table 1). In this case, the frontier molecular orbital theory proposed by Fukui could make some revision and gave a more reasonable conclusion [26]. According to the theory, reaction selectivity should be related to HOMO, LUMO and the orbits nearby. When the occupied orbit held higher energy level and meanwhile distributed around the related atom, this atom would be most likely the reaction position (Fig. 3). For 5-Br and 5-OCH_3 systems, the activity of 3-position comes from the distribution of HOMO in which heteroatom (S) contributed more electron to 3-position. This is also the reason for the higher activity of thiophene ring.

The isosurface and contour of f^- could intuitively show the sites with more net surplus of electronic distribution density. Electrophilic reagent usually tends to attack at the site (marked with

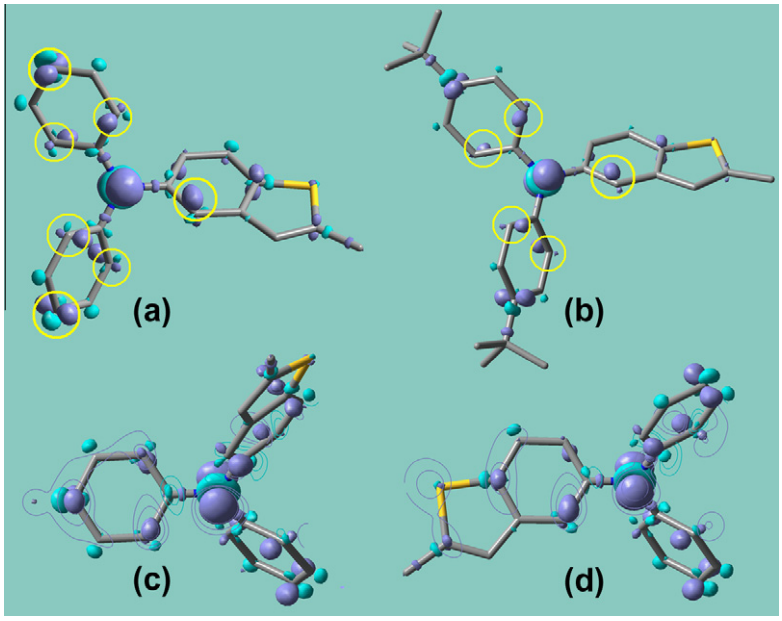


Fig. 4. Isosurface and contour of f^- for compound **2** and **3**. (a) The f^- isosurface of compound **2**, iso-value = 0.003, the yellow circle marks the possible reaction position or the "abnormal" reaction selectivity. (b) The f^- iso-surface of compound **3**, iso-value = 0.0026, the yellow circle marks the possible reaction position. (c) The contour (benzene ring) of compound **2**. (d) The f^- contour (benzothiophene ring) of compound **3**. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

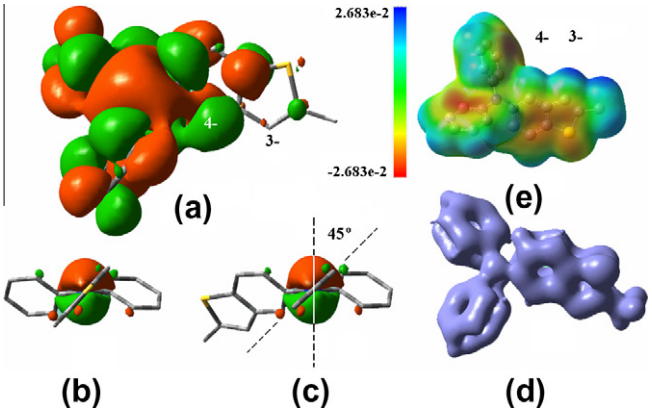


Fig. 5. Electron distribution of compound **2.** (a) The isosurface of the "interfinger-like" HOMO (orbital No. 83) of compound **2**, isovalue = 0.004. (b) The tilt of the most part of HOMO and the plane of benzo[b]thiophene when viewed at isovalue = 0.04. (c) The tilt of the most part of HOMO and the plane (C17–C22, benzene ring) of one of the two benzene rings when viewed at isovalue = 0.04; The tilt angle is about 45°. (d) Electron delocalization through π-orbits, isovalue = 0.023. (e) Electrostatic potential map.

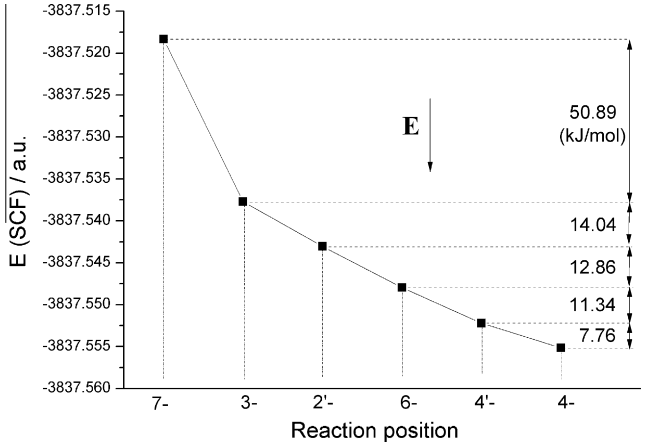
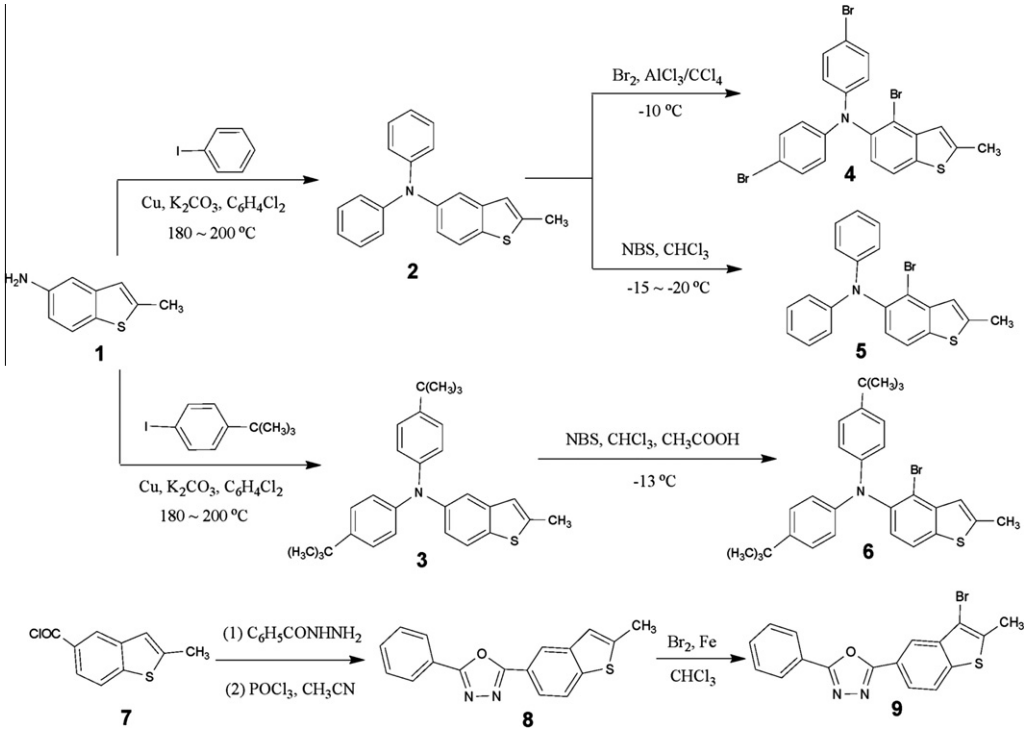


Fig. 6. Total energy of σ-complexes (in atom unit).

circle). For 5-diarylamino-2-methylbenzo[b]thiophene, there was not only one possible site in the bromination. 4-, 4′-, 3-, 2′- and 6-positions were the competitive positions. In Fig. 4, it could be found from the isosurface and contour of f^- that 6- and 3-positions were less active, but 4-, 4′- and 2′-positions (*o*- and *p*-of the N atom) more active. If the reaction was carried out at lower temperature and lower active bromination reagent was used, more selectivity would be expected. In this sense, reaction selectivity was really "abnormal".

In most cases, the N atom of amino group commonly tended to stay in sp^3 hybridization (triangle cone conformation) or in between sp^3 and sp^2 (such as in aniline). According to the calculation results, 5-diarylamino-2-methyl-benzo[b]thiophene existed in windmill-like structure, which had been confirmed by the X-ray diffraction data of 2-methyl-4-bromo-5-bis(4-tertiary butylphenyl) aminobenzo[b]thiophene **6** and some reported works. The HOMO had 99.99% of *p* orbital component (Figs. 4c and 5a) with 86.13% of occupation ratio, which was occupied by the lone pair electrons of N atom. However, the occupation of N atom in TPA was fairly lower. In other word, the N atom adopted sp^2 hybridization and 13.87% of the occupation shared with other atoms, so that the value of valence of the N atom was more than 3, reaching 5.47. Except for the three σ-bond, there were some additional bonds between the N atom and linked C atoms. It was the main difference between diarylamino in TPA structure and common amino. In 5-diarylamino-2-methylbenzo[b]-thiophene, the N atom as a center and the three bonded C atoms lied in a plane as show in Fig. 4. But, the three aromic rings and the center N atom were in windmill-like conformation. In the HOMO shown in Fig. 5b and c, there were about 45° tilt angle between the plane and linked



Scheme 1. Synthesis of related compounds.

aromic rings. As a result, the aromic rings were approximately vertical. Viewed from the distribution of the orbit, it was even more incredible that this type of orbit did not have face symmetry if iso-value was made to enough small to show the more complete view. So that, the HOMO was named "interfinger-like" orbit (Fig. 5a). It seemed to be not easy to form normal $p–\pi$ conjugate. In normal $p–\pi$ conjugate, the symmetry axis of p orbit and the aromatic ring ought to be perpendicular to each other so that the greatest degree of overlap could achieve. It was absolutely not the ordinary $p–\pi$ conjugation. In other words, a special no-planar conjugated model may exist in this system. In the model, electrons could still delocalize among the three aromatic rings (Fig. 5d). As a result, 4-, 6-, 2′- and 4′-positions all could gain the electron donation from N atom. These positions held more distribution of net negative charge ($\Delta\rho_i$) as shown in Figs. 3 and 4c and d. In addition, the electrostatic potential map (Fig. 5e) also revealed that 4-position is more vulnerable to be attacked by electrophillic reagent than 3-position.

As it is known, the σ-complex was the active intermediate formed in the process of electrophilic substitution. According to Hammond Postulate, the energy level of σ-complex reflects the level of active energy. Active energy is the primary factor to determine the selectivity. The total energy of related σ-complexes can be evaluated by calculation based on optimized structures (Fig. 6). Compared with any other σ-complexes, 4-Br–σ-complex had lowest energy (about -3837.55514 atom unit).

2.2. Synthesis and structural characterization

In order to verify the calculation results, the bromination of 5-diarylamino-2-methylbenzo[b]thiophene was carried out via Scheme 1. Some substrates for bromination, 2-methyl-5-diphenyl-amino benzo[b]thiophene (compound **2**), 2-methyl-5-bis (4-tert-butylphenyl)amino-benzothiophene (compound **3**), and 2-(2-methylbenzo[b] thiophen-5-yl)-5-phenyl-1, 3, 4-oxadiazole (compound **8**) had been synthesized and characterized in our previous works.

When bromination was run at lower temperature with less active reagents used, the selectivity of reaction could be clearly observed. Under the condition of $Br_2/AlCl_3$, −10 °C and non-polar solvent (CCl_4), Br atoms were introduced in both 4- and 4′-positions. Compound **4** was obtained as solid power. However, the growth of its single crystalline was unsuccessful. For less active reagents (NBS), only 4-Br product (compound **5**) was obtained as sticky solid without complete solidification upon standing. But the single crystalline of compound **6**, an analogue of compound

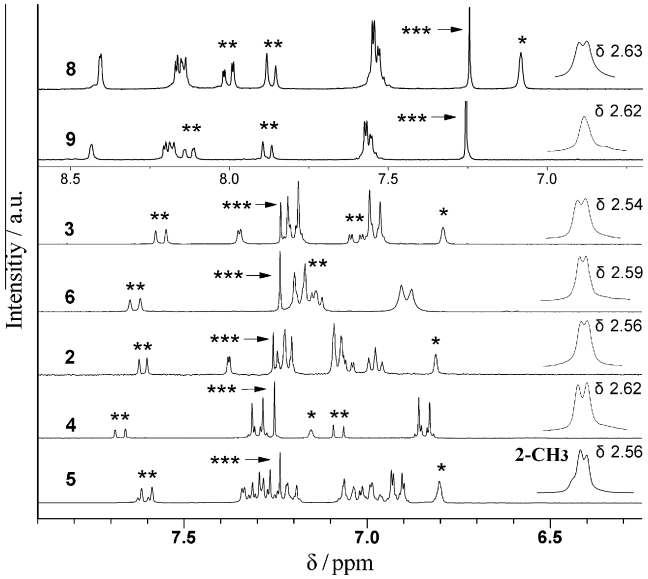


Fig. 7. ^{1}H NMR of compounds **2**, **3**, **4**, **5**, **6**, **8** and **9** * the peaks resulting from the H's at 3-position; ** the peaks resulting from the H's at 6- and 7-position; *** the peaks resulting from $CHCl_3$.

5, was obtained in petroleum ether. Compound **9** had also been synthesized as a reference of 3-Br product. Due to the electron-withdrawing effect of oxadiazole ring in 5-position, Br atom could be introduce to 3-position (in thiophene ring) for certain. Its ^{1}H NMR, as a reference of 3-Br product, could be used to compare with the ^{1}H NMR of 4-Br products to confirm the position of Br atom.

^{1}H NMR spectrums of related compounds (**2–6**) were shown in Fig. 7. The three H protons at 6-, 7- and 3-positions were easy to be distinguished. 6-H and 7-H gave two double peaks (marked "**") with a large interval. For example, compound **4** gave an interval of 178.59 Hz and relatively large coupling constants (J = 8.39 Hz). 3-H was a "lone" proton and usually gave a single peak. In addition, the peaks at about δ = 2.6, derived from the H atoms at 2-CH_3 of thiophene rings, were split into a double peak for compounds **2–6**. It should be attributable to the coupling between the H atoms at 2-CH_3 and 3-H ($^4J_{H-H}$ = 1–1.14 Hz). If the reaction occurred at 3-position, the coupling would disappear as shown in Fig. 7 (compound **9**). All the 4-Br products would retain the coupling.

In addition, the structure of compound **6** was characterized by single crystal X-ray diffraction. It was found that Br atom was linked with the C atom at 4-position (benzene ring) of benzo[b]

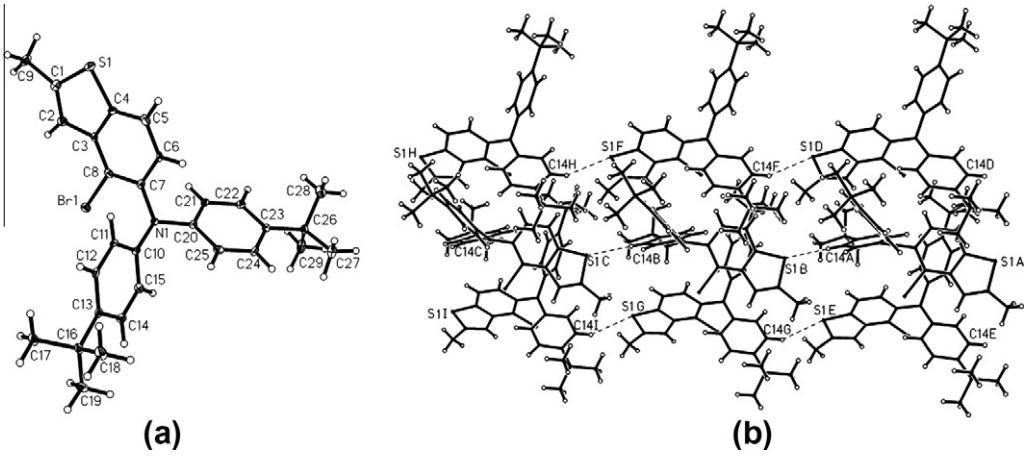


Fig. 8. (a) Molecular structure of compound **6** at 30% probability displacement ellipsoids. (b) Molecular packing of compound **6** viewed along *a* axis. Hydrogen bonds are showed as dashed lines.

thiophene in Fig. 8. It presented the windmill-like structure, which was also confirmed just as some previous studies [27]. The dihedral angles of phenyl rings (C10–C15) and (C3–C8) with benzene ring (C20–C25) are 59.7° and 79.9°, respectively. The thiophene ring (C1–C4/S1) and phenyl ring (C3–C8) are almost coplanar with their dihedral angle of only 1.8°, and the dihedral angles of phenyl rings (C3–C8) and (C10–C15) are approximately vertical with their dihedral angle of 90.5°, which is identical with theory calculation. In the crystal structure of **6**, molecules are linked through intermolecular C14–H14···S1 ($-x$, $y + 1/2$, $-z$) hydrogen bonds, forming chains running along *a* axis (Fig. 8b). Crystallographic data for the structures and the resulting table of crystalline data analysis are available from Supplementary data.

3. Conclusions

When diarylamino was in the 5-position of benzothiophene, molecular simulations and experiments had shown that bromination of the molecule was more possible to occur in 4- or 4′-position, rather than 3-position. Single crystal X-ray diffraction of compound **6** had given conclusive evidence. The selectivity was "abnormal" for general 5-substituted-2-methyl-benzo[b]thiophene with simple 5-substitutes. In the molecules, the N atom in TPA unit rather than thiophene ring may be the main factor for the selectivity. The fundamental reason was that the HOMO of the substrate held a special form of electron distribution around N atom so that a special "non-planar" conjugated system formed. The N atom adopted the configuration of the plane triangle (sp^2 hybridization), instead of the triangular cone (sp^3 hybridization). The orbit that the lone pair of the N atom occupied was not a pure *p*-orbital, but a unique "interfinger-like" orbit. Electrons were donated to the *o*- and *p*-position of linked aromatic rings by this manner of electron delocalization, so that 4- or 4′-position became the more active site. According to calculation, 4-Br-σ-complex contained the lowest energy, where 4-Br product would be the main product controlled by reaction kinetics factors.

4. Experimental

4.1. Materials and measurements

All chemicals were commercially available with AR grade and used without further purification. The melting point was determined by an XPR-201 microscopic melting apparatus and uncorrected. Elemental analysis was performed on Elementar Vario EL apparatus. ^{1}H NMR spectra were recorded on a Bruker AV300 instrument at 300 MHz in $CDCl_3$. HRMS were recorded on Finnigan MAT 95 mass spectrometer.

X-ray diffraction data were collected using a Bruker SMART-1000 CCD area detector equipped with a graphite mono-chromatized Mo Kα (0.71073 Å) radiation at 113(2) K. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares procedure with SHELXS-97 [28] and SHELXL-97 [29]. All hydrogen atoms were located in a difference Fourier map and their geometry was idealized, and refined by a riding model.

4.2. Bromination of 5-substituted-2-methylbenzo[b]thio-phene

4.2.1. 4-Bromo-N, N-bis(4-bromophenyl)-2-methylbenzo[b]thiophen-5-amine 4

Firstly, 5-diphenyl-2-methylbenzo[b]thiophene-amine **2** was prepared through the reaction of 2-methylbenzo[b]-thiophen-5-amine **1** (0.5 g, 3.06 mmol) with iodobenzene (1.5 g, 7.35 mmol) in 1, 2-dichlorobenzene. Iodobenzene was commercially available. The residue was treated with aluminum oxide microspheres and concentrated to obtain a pale yellow solid (0.65 g, 67%), m.p 136.0–140.0 °C. Anal. Calcd. (%) for $C_{21}H_{17}NS$: C, 79.96; H, 5.43; N, 4.44. Found (%): C, 79.82; H, 5.46; N, 4.47. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 7.61 (d, *J* = 8.60 Hz, 1H), 7.38 (d, *J* = 2.05 Hz, 1H), 7.23 (m, 4H), 7.08 (dd, *J* = 8.45, 0.86 Hz, 4H), 7.05 (dd, J_{H-H} = 8.66, 2.17 Hz 1H), 6.98 (t, *J* = 7.33, 7.33 Hz 2H), 6.81 (s, 1H), 2.56 (d, $^4J_{H-H}$ = 0.98 Hz, 3H).

2-Methyl-N, N-diphenylbenzo[b]thiophen-5-amine **2** (0.1 g, 0.30 mmol), and anhydrous $AlCl_3$ (44.6 mg) in CCl_4 (8.0 mL) were cooled to below −13 °C in ice-salt bath. A solution consisting of Br_2 (0.056 mL, 1.09 mmol) in CCl_4 (10 mL) was added dropwise slowly and stirred for 30 h. Then, the mixture was washed several times with 10% aqueous sodium carbonate and water. The organic phase was dried over magnesium sulfate and then concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with petroleum ether/$CHCl_3$ (10:1) to give slightly yellow solid (93.5 mg, yield 56.5%). Anal. Calcd. (%) for $C_{21}H_{14}Br_3NS$: C, 45.68; H, 2.56; N, 2.54; Found (%): C, 47.01; H, 2.60; N, 2.45. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 7.38 (dd, *J* = 178.59, 8.38 Hz, 2H), 7.29 (d, *J* = 8.92 Hz, 2H), 7.29 (q, *J* = 5.28, 5.28, 5.28 Hz, 2H), 7.17–7.13 (m, 1H), 6.83 (d, *J* = 8.92 Hz, 2H), 6.83 (q, *J* = 5.27, 5.27, 5.26 Hz, 2H), 2.61 (d, $^4J_{H-H}$ = 1.14 Hz, 3H). HS-ESIMS: *m*/*z* 548.8397, found 549.8473 (M + H$^+$, 100%).

4.2.2. 4-Bromo-N, N-diphenyl-2-methylbenzo[b]thiophen-5-amine 5

N-bromosuccinimide (NBS) (3.9 g, 21.7 mmol) was dissolved in a solution of acetated acid (45.0 mL) and $CHCl_3$ (80.0 mL). 2-methyl-N, N-diphenylbenzo[b]thiophen-5-amine **2** (5.0 g, 15.9 mmol) in a solution of $CHCl_3$ (150 mL) was added drop-wised to the above solution below −13 °C in 1 h. The result mixture was washed with water and neutralized with sodium carbonate to basicity. After concentration, the crude solid was purified by column chromatography on silica gel with petroleum ether (60–90 °C) to give colorless sticky compound **5** (6.1 g, yield 97.3%). Anal. Calcd. (%) for $C_{21}H_{16}BrNS$: C, 63.96; H, 4.09; N, 3.55; Found (%): C, 63.80; H, 4.00; N, 3.60. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 7.60 (d, *J* = 8.40 Hz, 1H, Ar–H), 7.34–7.24 (m, 4H, Ar–H), 7.22–7.19 (d, *J* = 8.39 Hz, 4H, Ar–H), 7.06–7.00 (m, 4H, Ar–H), 6.93–6.91 (dd, 2H, Ar–H), 6.80 (s, 1H, Ar–H), 2.56 (d, $^4J_{H-H}$ = 1.14 Hz, 3H, –CH_3). HS-ESIMS: *m*/*z* 393.0187, found 394.0262 (M + H$^+$, 100%).

4.2.3. 4-Bromo-5-bis(4-tert-butylphenyl)-2-methylbenzo[b]thiophene amine 6

Firstly, 5-bis(4-tert-butylphenyl)-2-methylbenzo-[b]thiophene amine **3** was prepared by the reaction of 5-amine-2-methylbenzo[b]thiophene **1** with 1-tert-butyl-4-iodo-benzene in 1, 2-dichlorobenzene. 1-tert-butyl-4-iodobenzene was commercially available or prepared from 4-tert-butylaniline. 5-amine-2-methylbenzo[b]thiophene was synthesized as a flake crystal (m.p. 56–58 °C) through several steps from 4-aminobenzenethiol [30–32].

2-Methylbenzo[b]thiophen-5-amine **1** (0.5 g, 3.06 mmol), 1-tert-butyl-4-iodobenzene (1.9 g, 7.30 mmol), 1,2-dichlorobenzene (10 mL), fresh treated Cu power (0.84 g, 200 mesh), fine power of anhydrous potassium carbonate (3.64 g) and 18-crown-6 (0.174 g) were added to 50 mL three-necked flask equipped with mechanical stirrer. The reaction mixture was stirred in N_2 for 48 h under reflux. The mixture was filtrated under vacuum and washed twice with hot 1, 2-dichlorobenzene. After steam distillation, residue 2-dichlorobenzene were removed. The resulting solid (1.45 g) was dissolved in petroleum ether (70 mL, 60–90 °C), then treated with aluminum oxide microspheres, and concentrated to obtain a pale yellow solid **3** (0.81 g, 62%), m.p 160–164 °C. Anal. Calcd. (%) for $C_{29}H_{33}NS$: C, 81.45; H, 7.78; N, 3.28. Found (%): C, 79.82; H, 7.97; N, 3.33. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 7.56 (d, *J* = 8.58 Hz, 1H), 7.35 (d, *J* = 2.03 Hz, 1H), 7.23–7.17 (m, 4H), 7.03 (dd, *J* = 8.59, 2.15 Hz, 1H), 7.01–6.94 (m, 4H), 6.79 (s, 1H),

2.54 (d, $^4J_{H-H}$ = 1.03 Hz, 3H), 1.29 (d, J = 4.88 Hz, 19H). HS-ESIMS: m/z 427.2334, found 428.2404 (M + H$^+$, 100%).

N-bromosuccinimide (NBS) (2.14 g, 16.5 mmol) was dissolved in a solution of acetated acid and $CHCl_3$. 2-methyl-5-bis(4-tertiary butylphenyl) amine-benzothiophene (5.0 g, 11.7 mmol) in $CHCl_3$ was added drop-wised to the above solution at below −13 °C in 1 h. The result mixture was washed with water and neutralized with sodium carbonate to basicity. After concentration, the crude solid was recrystallized in $CHCl_3$ to obtain pale yellow compound **6** (5.1 g, yield 86%), m.p. 199.5–202.8 °C. The pale yellow single crystal of **6** with long stick was obtained in petroleum ether at room temperature for 2 weeks. Anal. Calcd. (%) for $C_{29}H_{32}BrNS$: C, 68.76; H, 6.37; N, 2.77. Found (%): C, 68.48; H, 6.24; N, 2.65. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 7.63 (d, J = 8.39 Hz, 1H), 7.22–7.11 (m, 6H, Ar–H), 6.89 (d, J = 8.66 Hz, 4H, Ar–H), 2.59 (d, $^4J_{H-H}$ = 0.98 Hz, 3H, CH_3), 1.28 (s, 18H, $6CH_3$). HS-ESIMS: m/z 505.1439 found 506.1512 (M + H$^+$, 100%).

4.2.4. 2-(3-Bromo-2-methylbenzo[b]thiophen-5-yl)-5-phenyl-1, 3, 4-oxadiazole 9

Compound **8** was firstly prepared from **7** and benzohydrazide through general method. Iron powder reduced (10.0 g) was added to the solution of 2-(2-methylbenzo[b]thiophen-5-yl)-5-phenyl-1, 3, 4-oxadiazole **8** (2.2 g, 7.5 mmol) in CH_2Cl_2 (100 mL). Bromine (1.0 mL, 19.5 mmol) in CH_2Cl_2 (50 mL) was added dropwise under reflux. The result mixture was refluxed for 30 min, washed with 10% aqueous sodium carbonate and several times with water. The organic phase was dried over magnesium sulfate and then concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with $CHCl_3/CH_3COCH_3$ (40:0.5) to give colorless solid (1.6 g, yield 57.3%), m.p. 171.0–175.4 °C. Anal. Calcd. (%) for $C_{17}H_{11}BrN_2OS$: C, 55.00; H, 2.99; N, 7.55; Found (%): C, 55.09; H, 2.65; N, 2.43. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = ppm 8.43 (s, 1H), 8.19 (dd, J = 6.57, 3.11 Hz, 1H), 8.13 (dd, J = 8.41, 1.32 Hz, 1H), 7.88 (d, J = 8.39 Hz, 1H), 7.56 (dd, J = 5.05, 1.86 Hz, 1H), 2.62 (s, 3H). HS-ESIMS: m/z 369.9775, found 369.9772 (M$^+$, 100%).

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Appendix A. Supplementary material

^{13}C NMR data of compounds are available as the supplementary data associated with this article can be found online. Crystallographic data for the structures reported have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 852439). These data can be obtained free of charge from www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internet) +44 1223 336 033; email: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2012.07.054.

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