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Synthesis, single crystal X-ray structure and optical properties of 3,4-dimethyl-dithieno[2,3-*b*:3′,2′-*d*]thiophene-7,7-dioxide

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Abstract—The synthesis of the title compound (**4**), starting from commercial 3-bromo-4-methylthiophene, is described. The single crystal packing mode of **4**, as well as the absorption and photoluminescence properties in solution and in the solid state are reported and analyzed in relation to those of the isomeric 3,5-dimethyl-dithieno[3,2-*b*:2′,3′-*d*]thiophene-4,4-dioxide (**7**). The different reactivities of **4** and **7** towards bromination are analyzed in the light of the results of ab initio B3LYP/6-31G* calculations on both compounds. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

Dithienothiophenes are of current interest because they may be used as building blocks for the synthesis of a variety of functional materials for electronic and photonic devices,[1,2] such as light emitting diodes,[2] organic thin film transistors,[3a,b] photovoltaic cells,[4] etc. Poly(dithienothiophenes) have also been actively investigated in recent years in view of their n-type semiconductor properties.[5]

The wide interest in these compounds has prompted the search for new and more efficient synthetic methods of preparation. Recently, improved methods for the synthesis of dithieno[3,2-*b*:2′,3′-*d*]thiophene[6–8] and some of its isomers[8] have been reported.

In the framework of our investigation on the photo and electroluminescence properties of thiophene oligomers,[2,9] we used 3,5-dimethyldithieno[2,3-*b*:3′,2′-*d*]thiophene-7,7-dioxide (compound **7**, Fig. 1) as the 'rigid-core' for the preparation of a series of thiophene based oligomers characterized by high photoluminescence in solution as well as in the solid state.[2] The synthesis of the new oligomers was based on the cross coupling of the 2,6-dibromo derivative of **7** with the appropriate aryl stannane (Stille coupling).[2,9]

In this paper we report an investigation on the synthesis, the single crystal X-ray structure and the optical properties of 3,4-dimethyl-dithieno[2,3-*b*:3′,2′-*d*]thiophene-7,7-dioxide (compound **4**, Fig. 1) aimed at checking the possibility to employ this compound as the building block for the preparation of a new class of photoluminescent thiophene based oligomers.

The rationale behind the choice of dithieno **4** as the targeted building block was that, owing to the fact that the terminal rings are joined by a bond connecting two carbons β to sulfur, it would be characterized by a lower degree of delocalization than its isomer **7**. In consequence, the oligomers having compound **4** as the rigid-core should be characterized by lower absorption and emission wavelengths than those having **7**. Moreover, we were interested in understanding the way through which compound **4** self-organizes in the solid state and how this organization affects the photoluminescence efficiency.

Figure 1. Molecular structure and numbering scheme of 3,4-dimethyl-dithieno[2,3-*b*:3′,2′-*d*]thiophene-7,7-dioxide (**4**) and of 3,5-dimethyl-dithieno[3,2-*b*:2′,3′-*d*]thiophene-4,4-dioxide (**7**).

Keywords: thiophene; X-ray; optical properties; ab initio calculations.

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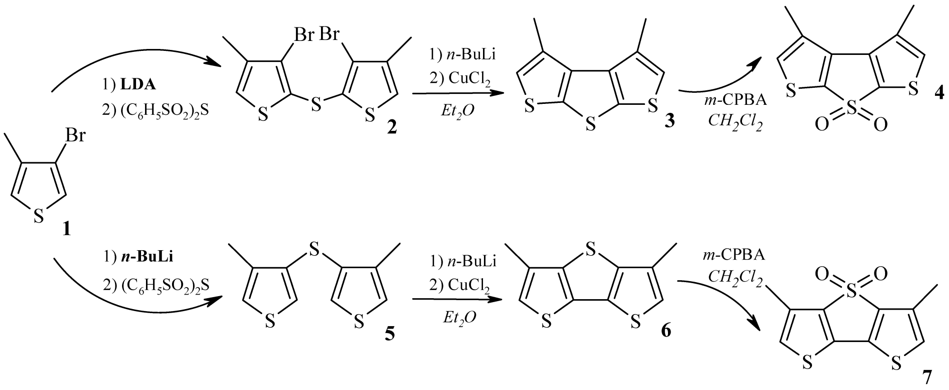


Scheme 1.

2. Results

2.1. Synthesis of 3,4-dimethyl-dithieno[2,3-*b*:3′,2′-*d*]thiophene-7,7-dioxide (4)

The synthetic pattern followed for the preparation of 3,4-dimethyl-dithieno[2,3-*b*:3′,2′-*d*]thiophene-7,7-dioxide **4**, starting from commercial 3-bromo-4-methylthiophene **1**, is reported in Scheme 1.

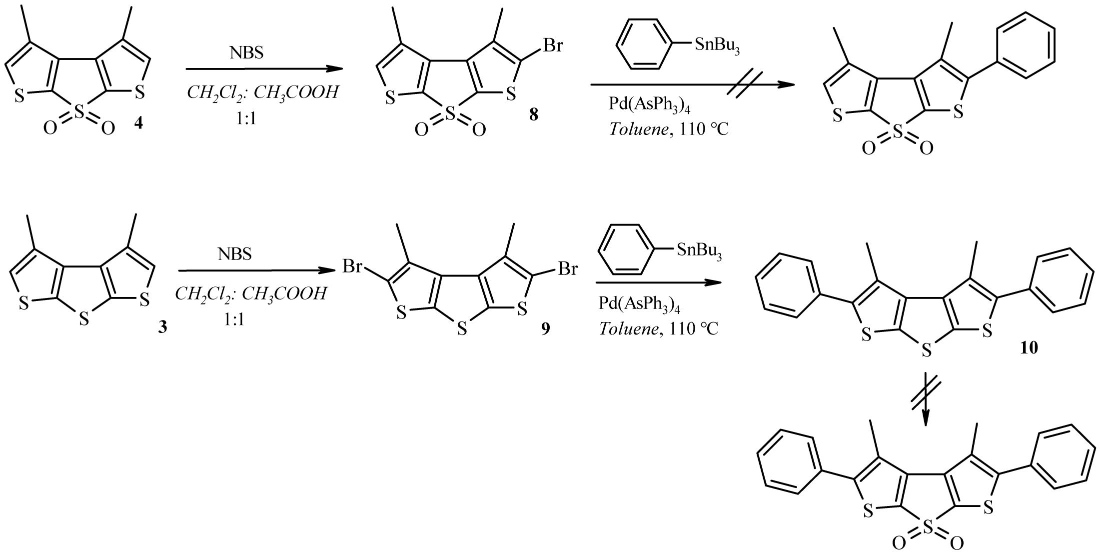
The procedure is similar to that described in 1971 for the preparation of the unsubstituted counterpart of **4**[10] and is reported in Scheme 1 together with the analogous preparation of the isomeric 3,5-dimethyl-dithieno[3,2-*b*:2′,3′-*d*]thiophene-4,4-dioxide **7**, for comparison.

The scheme shows that lithiation of **1** using lithium diisopropylamide leads to the removal of the proton next to bromine. The subsequent reaction of the carbanion with bis(phenylsulfonyl) sulfide leads to the formation of (3-bromo-4-methyl)-(2)-thienyl sulfide **2**. The action of *n*-butyllithium on compound **2**, followed by $CuCl_2$ mediated oxidative ring closure, leads to the formation of dithieno[2,3-*b*:3′,2′-*d*]thiophene **4**.

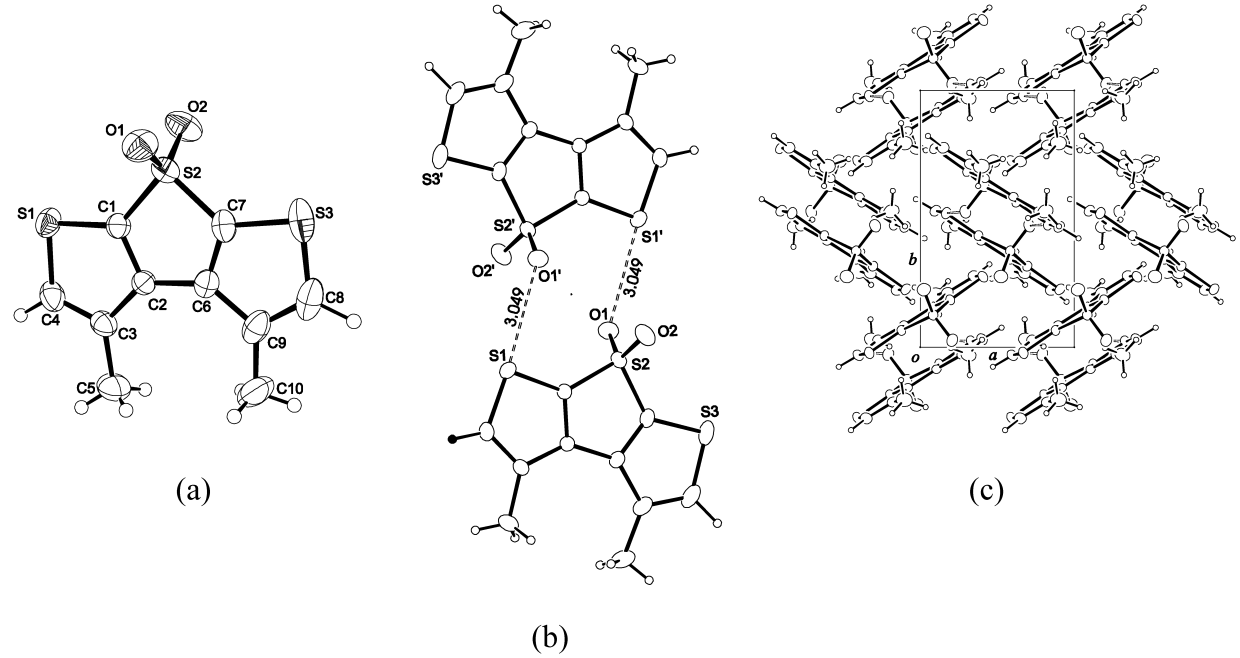
If, in the first step of the reaction, *n*-butyllithium is used instead of LDA, it is the bromine atom that is removed and subsequent work up with the same modalities leads to the formation of **7**.[2]

Reaction of *S*,*S*-dioxide **4** with 2 equiv. of NBS in a 1:1 mixture of dichloromethane/acetic acid afforded the monobromo derivative **8**, as shown in Scheme 2. Further attempts to brominate the second terminal position next to sulfur in different solvents (DMF, CH_2Cl_2, CH_2Cl_2/CH_3COOH) were unsuccessful, contrary to what we observed previously with compound **7**.[2] Moreover, the Stille coupling between monobromo **8** and phenyl stannane, using the same modalities employed to obtain the oligomers containing the rigid-core **7**,[2] did not take place. Not only the desired oligomer was not obtained but only traces of starting materials were recovered.

Dibromination of 3,4-dimethyl-dithieno[2,3-*b*:3′,2′-*d*]thio-



Scheme 2.



(a) (b) (c)

Figure 2. Molecular structure, dimeric arrangement and crystal packing of compound **4**.

phene **3** with 2 equiv. of NBS in the same solvent afforded the 2,5-dibromide **9** (Scheme 2). However, we failed in trying to oxidize the central sulfur of **10** to the corresponding *S*,*S*-dioxide by the use of *m*-CPBA in methylene chloride, as a mixture of several different products was obtained from which we were unable to identify the desired compound.

2.2. Single crystal X-ray structure of 3,4-dimethyldithieno[2,3-*b*:3′,2′-*d*]thiophene-7,7-dioxide 4

The crystal structure of compound **4**, built up of one crystallographically independent molecule, is presented, along with atom numbering scheme, in Figure 2(a). Some relevant structural features are reported in Table 1.

Bond distances and angles compare very well with those observed in other fused-ring oligothiophene *S*,*S*-dioxides. Nevertheless, there are some small but significant differences in bond length of inner thiophene ring of **4** and that of its isomeric 3,5-dimethyldithieno[3,2-*b*:2′,3′-*d*]thiophene-4,4-dioxide derivative **7**.[2] The most relevant one involves the C2–C6 (Fig. 2(a)) bond, lengthened from 1.450(3) Å in **7** to 1.481(2) in **4**. At the same time, there is slight lengthening of the adjacent C–C bonds (mean value 1.370(2) Å in **7** and 1.376(2) Å in **4**), and shortening of C–S bonds, whose mean value is 1.762(2) Å in **7** and 1.750(2) Å in **4**.

The most relevant and somewhat surprising structural feature of compound **4** is, in our opinion, its molecular packing, completely different from those previously observed in other oligothiophene *S*,*S*-dioxides.[2] Two molecules, related by an inversion center and hence parallel, interact through two extremely short π–π contacts between one sulfonic oxygen atom and one thienyl sulfur, giving rise to dimeric pairs (see Figure 2(b)). The S···O separation of 3.049(1) Å is noticeably shorter than those (from 3.263 to 3.298 Å) observed in other rigid-core oligothiophene dioxides.[2]

Table 1. Summary of relevant structural features of compound **4**

C–S (Å)		S–O (Å)		C–C (Å)		C1–C2[a]	C7–C6[a]
Outer rings	Inner rings	Outer rings	Inner rings	Outer rings	Inner rings		
1.697(2)	1.747(1)		1.433(1)	1.426(2)	1.481(2)[b]	1.377(2)	1.375(2)
1.710(2)	1.752(2)		1.429(1)	1.365(2)			
1.698(2)				1.434(2)			
1.712(3)				1.368(2)			
Max out of plane (Å) of ring atoms	−0.041(2)						
Out of plane (Å) of O atoms	1.184(2)	−1.259(2)					
Shortest intermolecular contacts (Å)	3.049(1)	O···S					
	3.493(3)	O···C					
	3.6425(6)	S···S					
Dihedral angles (deg) molecules related by glide plane	65.88(2)						

[a] See Figure 2(a).

[b] Bond C2–C6 in Figure 2(a).

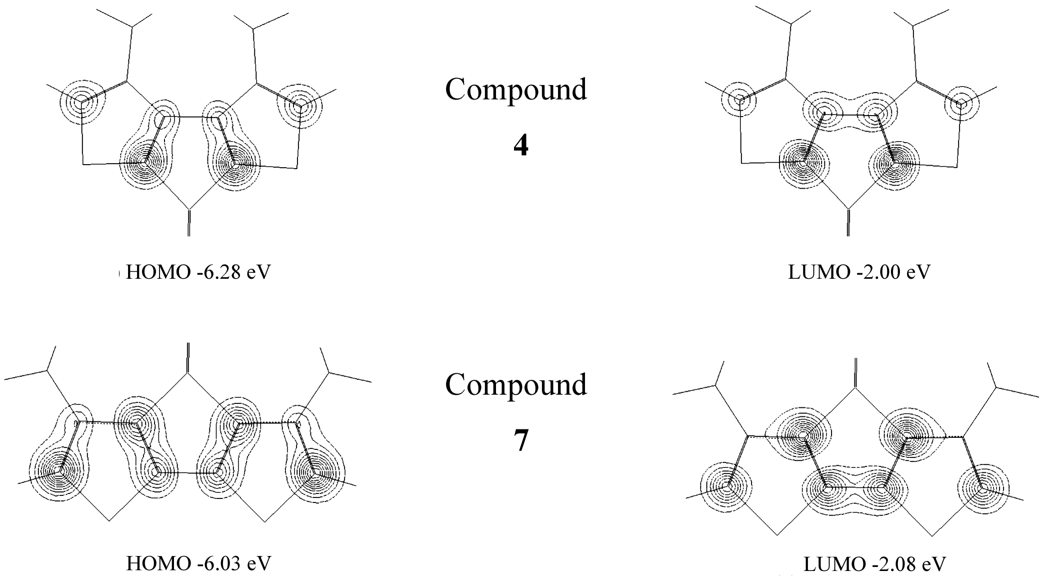


Figure 3. B3LYP/6-31G* electronic densities and energies of the frontier orbitals of compounds **4** and **7**.

Rather surprisingly, the second sulfonic oxygen atom of compound **4** is not involved in any significantly short non-bonded interactions. On the contrary, in the above cited dioxides, both sulfonic oxygens participate in short intermolecular interactions, which lead to complex tridimensional networks. In compound **4** the dimeric pairs pack in the crystal (Fig. 2(c)) in a way very close to the herringbone packing motif, commonly observed in planar unsubstituted oligothiophenes.[11] In this case, the herringbone angle would be 65.88(2)°. Only another short and perhaps significant intermolecular contact, involving thienyl S atoms at 3.6425(6) Å, is present in the crystal packing of **4**.

2.3. Theoretical calculations

Ab initio B3LYP/6-31G* calculated electronic densities and energies of the HOMO and LUMO frontier orbitals of compounds **4** and **7** are shown in Figure 3.

Figure 3 shows that the symmetry of the frontier orbitals of compounds **4** and **7** is the same: the HOMO is characterized by A2 symmetry and the LUMO by B1 symmetry.

However, the electronic densities (as measured by the square orbital coefficients) and the HOMO–LUMO energies of **4** are different from those of **7**. While in **4** most of the electronic density is located on the inner ring, in **7** the electronic density is better distributed over the whole molecular skeleton. In both systems, the electronic density on the sulfur atoms is very low. Moreover, the frontier orbital energies of **4** are lower than those of **7**, particularly the HOMO energy.

Ab initio B3LYP/6-31G* calculations on compounds **4** and **7** brominated at one of the terminal positions showed that the frontier orbitals retain their symmetry but that their energies change in a different manner. LUMOs are more affected than HOMOs by bromine substitution and in particular the HOMO energy of **4** remains almost the same (HOMO energy: −6.3 and −6.04 eV for **4** and **7**, respectively. LUMO energy: −2.17 and −2.26 eV for **4** and **7**, respectively).

2.4. Optical properties

Table 2 shows the maximum absorption (λ_{max}) and emission (λ_{PL}) wavelengths and the photoluminescence quantum efficiencies (PLQE) of compound **4** together with those of **7**, for comparison. Figure 4 shows the absorption spectra of **4** and **7** in solution and Figure 5 the photoluminescence spectra of **4** in solution and in thin film.

The Table and the Figures show that there are marked differences in the optical properties of the two compounds. In particular, the photoluminescence efficiency (η) of **4** is much smaller than that displayed by **7**, in solution as well as in the solid state. Moreover, the η value of **4** in solution is the same as that in thin film, while the corresponding values in **7** are sizably different. Finally, in solution the measured Stokes shift between the absorption and emission peak is larger in compound **4** than in **7** (Table 2 and Fig. 5).

As shown in Figure 4, the absorption spectrum of **4** in solution is characterized by the presence of an intense and structured band near 300 nm and by a broad and much

Table 2. Maximum absorption (λ_{max}, nm) and emission (λ_{PL}, nm) wavelengths and photoluminescence quantum yields (η, %) of compounds **4** and **7**.

Compound		λ_{max}	λ_{PL}	η
4	Solid[a]	[b]	500	4
	Solution[c]	310, 349	490	4
7	Solid[d]	360	518	16
	Solution[c]	364	457	77

Absolute values measured using an integrating sphere.

[a] Spin-coated film.

[b] The spectrum shows bands near 300 and 340 nm with an intense tail ending near 600 nm.

[c] CH_2Cl_2.

[d] Microcrystalline powder.[2]

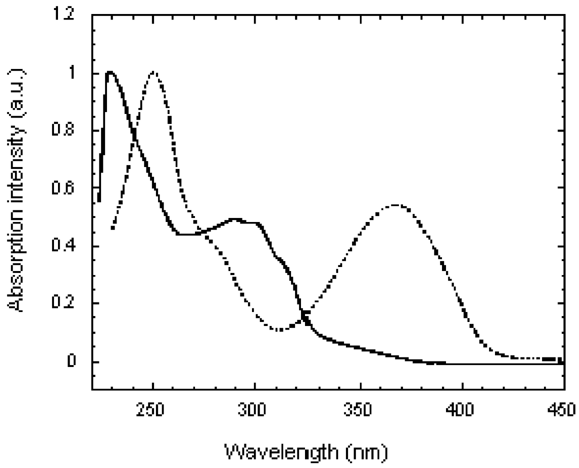


Figure 4. Normalized absorption spectra of compound **4** (solid line) and **7** (sketched line) in solution.

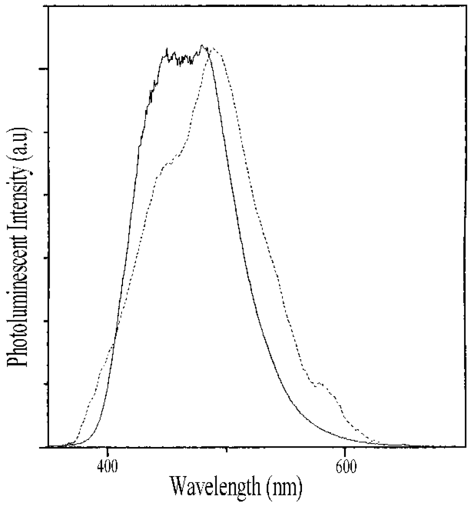


Figure 5. Normalized photoluminescence spectra of **4** in solution (solid line) and in thin film (sketched line).

weaker band around 350 nm, whereas the corresponding spectrum of **7** shows the presence of an intense featureless band at 364 nm.

To account for the marked differences in the absorption spectra of **4** and **7**, we carried out ZINDO/S calculations, using the B3LYP/6-31-G* optimized geometries. According to ZINDO/S calculations, for both compounds the HOMO and LUMO orbitals are π in character and very similar to those obtained by ab initio calculations. The NEXT HOMO and the NEXT LUMO orbitals are σ in character, involving essentially the sulfonic group in the NEXT HOMO and the entire skeleton in the NEXT LUMO. The highest wavelength band in the absorption spectrum of dithienothiophene **4** is the symmetry forbidden HOMO–NEXT LUMO $\pi-\sigma^*$ transition at 349 nm. The HOMO–LUMO $\pi-\pi^*$ transition does not appear because it is mixed up with the NEXT HOMO–NEXT LUMO $\sigma-\sigma^*$ transitions leading to two bands at 330 and 261 nm in which the oscillator strengths are almost zeroed by mutual annulment. Then a transition from the HOMO to a higher energy σ^* orbital gives rise to a partially forbidden band at 299 nm (oscillator strength 0.012). The most intense absorption bands at 255 and 247 nm come from transitions involving the HOMO or LUMO and further π^* or π orbitals.

Concerning dithienothiophene **7**, ZINDO/S calculations indicate that the absorption spectrum is made of two intense bands at 369 and 271 nm. The former is the pure HOMO–LUMO $\pi-\pi^*$ transition, while the latter is the pure NEXT HOMO NEXT LUMO $\sigma-\sigma^*$ transition.

The calculations are in agreement with the single crystal X-ray geometry of compound **4**, according to which (Table 1) the carbon–carbon bond linking the terminal thienyl rings in **4** (1.481 Å) is much longer than that linking the terminal rings in **7** (1.450 Å)[2] and has, in consequence, a lower double bond character. The lower degree of conjugation of **4** compared to **7** is also in agreement with the fact that the absorption bands of the former compound are blue shifted with respect to those of the latter (Fig. 4).

3. Discussion

As shown in Scheme 1, starting from 3-bromo-4-methylthiophene it is possible to obtain either sulfides **2** or **5**, depending on the base employed in the first step of the reaction. Use of the more basic *n*-BuLi leads to removal of the bromine atom, while use of the less basic but more nucleophilic LDA leads to removal of the α-proton next to bromine. Consequently, the subsequent action of $(C_6H_5SO_2)_2S$ causes the formation of **2** or **5**. The reaction of **2** and **5** with *n*-BuLi/$CuCl_2$ leads to ring closure and formation of dithienothiophes **3** and **6**, respectively. In both cases, the ring closure occurs with relatively low yields: 47% for **3** and 60% for **4**[2] (isolated yields), comparable to those reported in the literature for the unsubstituted counterparts.

The action of *m*-CPBA on dithienothiophene **3** leads to the selective oxidation of the internal thienyl sulfur to give the corresponding *S*,*S*-dioxide, in reasonably good yield (68%), comparable to that already obtained for the preparation of compound **7**.[2]

However, the behaviour of dithienothiophene *S*,*S*-dioxide **4** towards bromination is very different from that of **7**,[2] as only the monobromo derivative **8** is formed by action of *N*-bromosuccinimide, even when much more than the stoichiometric amount of NBS was employed in several different solvents. Moreover, attempts to carry out Stille coupling between monobromo **8** and tributylphenylstannane were unsuccessful (Scheme 2).

To bypass the difficulties in the bromination of *S*,*S*-dioxide **4**, we decided to brominate dithienothiophene **3** and to prepare the *S*,*S*-dioxide in the subsequent steps. As shown in Scheme 2, the dibromination of **3** with NBS was successful (48% isolated yield), as well as the Stille coupling between the dibromo derivative and tributylphenylstannane to afford oligomer **10** (51% isolated yield). Unfortunately, the oxidation of **10** with *m*-CPBA was no more selective and a series of differently S,S-oxidated oligomers was recovered.

From these results we can conclude that the reactivity of **4** is very different from that of **7** and that alternative ways have to be explored in order to build up a new class of oligomers with **4** as the internal rigid-core.

Ab initio B3LYP/6-31G* calculations suggests that the different behavior of **4** and **7** towards bromination might be related to the different HOMO energy of the two compounds. Indeed, the HOMO energy of **4** is sizably higher than that of **7**, as shown in Figure 3; moreover, the calculations show that energy gap between the two monobromo derivatives is even larger.

Photoluminescence efficiency (number of photons re-emitted radiatively to the photons absorbed) depends on the competition between radiative and non-radiative patterns for energy relaxation to the ground state upon photoexcitation. Dithieno derivative **7** is characterized by high PL efficiency in solution, more than two orders of magnitude greater than that of oligomers containing the thienyl-*S*,*S*-dioxide moiety.[2,9a,12] On the contrary, as shown in Table 2, the photoluminescence efficiency of dithieno derivative **4** in solution is almost twenty times lower than that of **7**.

The type of theoretical calculations employed in this work do not allow an accurate description of the excited states and then of the photoluminescence characteristics of compound **4**. Nevertheless, according to Kasha's empirical rule,[13] the luminescence of isolated molecules originates from the radiative decay of the lowest excited state, which is correlated to the lowest energy absorption state. Thus, the different PL properties shown by **4** with respect to **7** in solution can reasonably be ascribed to the different nature of the absorption and emission states involved in the transition. Apparently, the intermolecular interactions related to packing in the solid state do not affect the PL efficiency of **4**, which is the same in solution and in the solid state, contrary to what is observed for compound **7**.[2]

4. Conclusion

The data reported in this paper show that dithieno thiophene **4** has reactivity, crystalline packing and photoluminescence properties that are very different from those of the isomeric dithieno thiophene **7** and make this compound less useful as building block for the preparation of molecular materials for electroluminescent devices.

5. Experimental

5.1. Synthesis of materials

General information. Organic solvents were dried by standard procedures. Analytical thin layer chromatographies (TLC) were carried out using 0.2 mm sheets of silica gel 60 F_{254} (Merck) and 0.2 mm sheets of aluminum oxide 60 F_{254} neutral (Merck); Flash chromatographies were carried out using silica gel 60 (230–400 mesh ASTM; Merck) and aluminum oxide 90 standardized (Merck). Stille reactions were carried out under nitrogen. 3-Bromo-4-methylthiophene, tributylphenyltin, and diisopropylamine were available from Aldrich; *n*-butyllithium, *N*-bromosuccinimide and copper(II)dichloride were obtained from Lancaster; sulfur dichloride from Carlo Erba; 3-chloroperbenzoic acid was available from Fluka. $Pd(AsPh_3)_4$ was prepared in situ from tris(dibenzylidene acetone)-dipalladium(0)-chloroform adduct (Aldrich) and triphenylarsine (Aldrich).[14]

The synthesis of 3,5-dimethyl-dithieno[3,2-*b*:2′,3′-*d*]thiophene-4,4-dioxide (**7**) has already been reported.[2]

5.1.1. (3-Bromo-4-methyl)-(2)-thienyl sulfide (2). To a solution of diisopropylamine (1.14 g, 1.58 mL, 0.011 mol) in ether (20 mL) *n*-butyllithium (4.52 mL, 0.011 mol, 2.5 M in hexanes) was added dropwise at −78°C. The mixture was allowed to warm to 0°C for 15 min and recooled to −78°C. To the above solution 3-bromo-4-methylthiophene (2.00 g, 1.26 mL, 0.011 mol) was added dropwise. The resulting mixture was stirred at this temperature for 2 h, and $(C_6H_5SO_2)_2S$ (1.73 g, 0.005 mol) was added in small portions over 30 min. The solution was allowed to warm to room temperature for 1 h. The mixture was poured into water and filtered through Celite. The aqueous layer was extracted with ether, and the organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography (silica gel, petroleum ether ethyl acetate) to give 1.10 g (51% yield) of product as pale yellow oil: MS *m*/*e* 384 ($M^{\cdot+}$); ^{1}H NMR ($CDCl_3$, TMS/ppm) δ 7.06 (q, 2H, ^4J=1.2 Hz), 2.21 (d, 6H, ^4J=1.2 Hz); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 137.97, 129.02, 124.43, 120.68, 16.93. Anal. calcd for $C_{10}H_8Br_2S_3$: C, 31.26; H, 2.10 Found: C, 31.33; H, 2.08.

5.1.2. 3,4-Dimethyl-dithieno[2,3-*b*;3′,2′-*d*]thiophene (3). *n*-Butyllithium (2.3 mL, 5.72 mmol, 2.5 M in hexane) was added over 15 min to a solution of **2** (1.10 g, 2.86 mmol) in 10 mL of dry ether at −78°C. The mixture was stirred at this temperature for 1 h, and then added dropwise via cannula to a solution of copper(II)dichloride (0.87 g, 6.50 mmol) in 15 mL of dry ether at −78°C. The mixture was allowed to warm to room temperature and was stirred overnight. The mixture was poured into water and filtered through Celite. The aqueous layer was extracted with ether, and the organic extracts were washed brine and dried over sodium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by flash chromatography (aluminum oxide, hexane) to provide 0.30 g (yield 47%) of the title product as white crystals. Mp 102–103°C; MS *m*/*e* 224 ($M^{\cdot+}$); λ_{max} (CH_2Cl_2) 254 nm; ^{1}H NMR ($CDCl_3$, TMS/ppm) δ 6.95 (q, 2H, ^4J=1.2 Hz), 2.62 (d, 6H, ^4J=1.2 Hz); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 139.65, 138.67, 130.02, 123.06, 18.37. Anal. calcd for $C_{10}H_8S_3$: C, 53.53; H, 3.59 Found: C, 53.45; H, 3.58.

5.1.3. 3,4-Dimethyl-dithieno[2,3-*b*;3′,2′-*d*]thiophene-7,7-dioxide (4). To a solution of **3** (0.30 g, 1.34 mmol) in 15 mL of dichloromethane was added 3-chloroperbenzoic acid (0.73 g, 2.9 mmol) in small portions. The mixture was stirred at room temperature overnight before washing sequentially with 10% KOH, 10% $NaHCO_3$ and brine. The organic layer was dried over sodium sulfate and the solvent was removed in vacuo. The crude product was purified by flash chromatography (aluminum oxide, hexane–ethyl acetate 8:2) to afford 0.23 g (68% yield) of the title compound as off-white microcrystals: mp 213–214°C; MS *m/e* 256 ($M^{\cdot+}$); λ_{max} (CH_2Cl_2) 310 nm; λ_{em} (CH_2Cl_2) 434 nm; FTIR (neat) 1165, 1298 cm^{-1}; ^1H NMR ($CDCl_3$, TMS/ppm) δ 7.22 (d, 2H, ^4J=1.2 Hz), 2.50 (d, 6H, ^4J=1.2 Hz); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 140.33, 139.70, 131.52, 131.08, 17.44. Anal. calcd for $C_{10}H_8O_2S_3$: C, 46.85; H, 3.15 Found: C, 46.82; H, 3.14.

5.1.4. 2-Bromo-3,4-dimethyl-dithieno[2,3-*b*;3′,2′-*d*]thiophene-7,7-dioxide (8). To solution of 0.30 g (1.2 mmol) of compound **4** in 10 mL of a 1:1 mixture of dichloromethane/acetic acid was added stepwise 0.43 g (2.4 mmol) of NBS at −20°C. After this addition, the cooling bath was removed and the mixture was allowed to warm to room temperature and stirred overnight before quenching with water. The aqueous layer was extracted with dichloromethane (3×40 mL), and the combined organic extracts were dried over anhydrous sodium sulfate. The crude product was recrystallized from toluene to afford 0.14 g (yield 34%) of the title product as a faint yellow solid: MS *m/e* 335 ($M^{\cdot+}$); ^1H NMR ($CDCl_3$, TMS/ppm) δ 7.52 (d, 1H, ^4J=1.2 Hz), 2.51 (d, 3H, ^4J=1.2 Hz), 2.19 (s, 3H); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 192.17, 151.56, 143.14, 141.92, 133.92, 133.65, 133.25, 83.89, 15.86, 12.24. Anal. calcd for $C_{10}H_7BrO_2S_3$: C, 35.83; H, 2.10 Found: C, 35.79; H, 2.08.

5.1.5. 2,5 Dibromo-3,4-dimethyl-dithieno[2,3-*b*;3′,2′-*d*]thiophene (9). Under exclusion of light, *N*-bromosuccinimide (0.16 g, 0.92 mmol) was added in small portions over 30 min to a solution of **3** (0.10 g, 0.46 mmol) dissolved in 10 mL of a 1:1 mixture of dichloromethane–acetic acid at 0°C. The mixture was allowed to warm up to room temperature and stirred overnight before quenching with water. The aqueous layer was extracted with dichloromethane, and the combined organic layers were washed with saturated aqueous sodium bicarbonate, water and brine. After drying over sodium sulfate the solvent was evaporated and the remaining residue was purified by column chromatography (SiO_2, hexane–dichloromethane 9:1) to provide 0.08 g (yield 48%) of the title compound as colorless microcrystals. Mp 228–229°C; MS *m/e* 382 ($M^{\cdot+}$); ^1H NMR ($CDCl_3$, TMS/ppm) δ 2.60 (s, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 137.64, 136.53, 129.93, 110.69, 17.67. Anal. calcd for $C_{10}H_6Br_2S_3$: C, 31.43; H, 1.58. Found: C, 31.45; H, 1.59.

5.1.6. 2,5 Diphenyl-3,4-dimethyl-dithieno[2,3-*b*;3′,2′-*d*]thiophene (10). In a flame-dried flask charged with a 2 mL toluene solution containing 0.02 mmol of $Pd(Ph_3As)_4$ formed in situ was added **9** (0.08 g, 0.22 mmol) in toluene (10 mL), then the mixture was heated to reflux and tributylphenyltin (0.16 g, 0.14 mL, 0.44 mmol) was slowly added by syringe. After this addition the reflux was continued for 2 h and stirred at room temperature overnight. The solvent was removed by rotary evaporation and the residue was purified by column chromatography (silica gel, cyclohexane) to provide 0.04 g (yield 51%) of the title compound as a colorless solid: mp 242–243°C; MS *m/e* 376 ($M^{\cdot+}$); ^1H NMR ($CDCl_3$, TMS/ppm) δ 7.50–7.43 (m, 8H), 7.40–7.35 (m, 2H), 2.66 (s, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 140.58, 140.16, 137.21, 135.07, 130.18, 128.68, 127.84, 125.96, 17.50. Anal. Calcd for $C_{22}H_{16}S_3$: C, 70.17; H, 4.28. Found: C, 70.20; H, 4.29.

5.2. X-Ray crystallography

$C_{10}H_8O_2S_3$; white, air stable crystals, grown by slow evaporation from pentane solution. The selected one had approximate dimensions 0.40 ×0.35×0.30 mm^3. All measurements were carried out at room temperature on a Enraf-Nonius CAD4 diffractometer, by using graphite-monochromated Mo Kα radiation (λ=0.71069 Å). Unit cell dimensions were obtained from least-squares fit to the setting angles of 25 automatically centred reflections in the 7–17° θ range. Crystals are monoclinic, $P2_1/n$ space group, with a=6.499(1), b=10.715(2), c=15.503(3) Å, β=96.34(1) and V=1073.0(4) $Å^3$. For Z=4 the calculated density is 1.587 mg/m^3. A total of 3770 reflections were collected in the 2.32–29.96° θ range in $\varpi-2\theta$ scan mode. Data were averaged to 3120 unique reflections (R_{int}=0.0241), of which 2497 had $I\geq 2\sigma(I)$. Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction, based on the ψ scan, was applied to data ($0.792\geq T_{factor}\geq 1.000$). The structure was solved by direct methods (SHELX86 program) and was refined through full matrix least-squares calculations based on F^2 (SHEXL93) for all unique reflections.[15,16] All non-hydrogen atoms were refined anisotropically and hydrogen atoms, located in ΔF maps, isotropically. Least-squares refinements of 164 parameters led to final $R1$ and $wR2$ values of 0.0323 and 0.0905, respectively, for reflections with $I\geq 2\sigma(I)$; corresponding values for all intensity data were 0.0435 and 0.0958. Largest peak and hole in a final ΔF map were 0.300 and −0.440 e $Å^{-3}$, respectively.

Crystallographic data (excluding structure factors) for the structure in this paper were deposited with the Cambridge Crystallographic Data Centre as supplementary material publication number CCDC 200051. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2, 1EZ, UK [fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

5.3. Theoretical calculations

Ab initio calculations were performed using the Gaussian98 series of programs.[17] The geometries were fully optimized by standard gradient techniques and the critical points checked by frequency analysis. Optimized coordinates are reported as Supporting Information. UV transitions were calculated by ZINDO/S-C.I. (10×10) single point calculations on ab initio geometries using HyperChem integrated package.[18]

5.4. Photoluminescence measurements

The photoluminescence spectra and quantum efficiency of compound **4** in the solid state was measured by placing a spin-coated film into a integrating sphere (Labsphere) and by exciting the sample with a He–Cd laser (λ=325 nm) under a flux of purging nitrogen to inhibit photo-oxidation. The PL signal was collected by means of a CCD spectrograph (Ocean Optics).

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