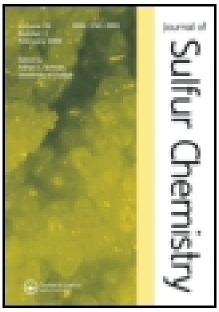

Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gsrp20

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Version of record first published: 20 Mar 2013.

To cite this article: Sule Taskiran Cankaya , Asli Capan , Mehmet Emin Cinar , Ezgi Akin , Sebahat Topal & Turan Ozturk (2013): Syntheses and properties of 3,4-diaryldithieno [2,3-b;3′,2′-d]thiophenes, Journal of Sulfur Chemistry, DOI:10.1080/17415993.2013.774400

To link to this article: http://dx.doi.org/10.1080/17415993.2013.774400

Journal of Sulfur Chemistry, 2013
http://dx.doi.org/10.1080/17415993.2013.774400

Syntheses and properties of 3,4-diaryldithieno [2,3-*b*;3′,2′-*d*]thiophenes

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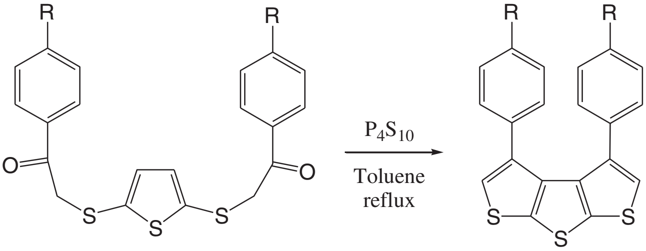
(*Received 30 December 2012; final version received 1 February 2013*)

Dithieno[2,3-*b*;3′,2′-*d*]thiophenes (DTT), having substituted phenyl groups at 3- and 4-carbons, have been synthesized, applying 2,5-diketone ring closure reaction using P_4S_{10}. Cyclic voltammetry studies indicated that all the DTTs had the oxidation potentials between 1.19 and 1.70 V. Computational calculations displayed positive radical spin densities at C2 positions for DTTs and negative for their dimers.



Keywords: dithienothiophenes; phosphorus decasulfide (P_4S_{10}); radical spin density; cyclic voltammetry; electropolymerization

1. Introduction

Dithienothiophenes (DTT) are formed by three fused thiophenes, which have six isomers, depending on the orientations of the thiophenes (*1*, *2*). They have been increasingly attractive due to their interesting properties in organic electronic materials (*3–5*). Presence of three sulfur atoms makes DTTs rich in electrons and good electron donor molecules, which are important properties for building blocks of wide variety of organic materials, having electronic and optical applications such as conducting polymers, electrochromic displays, electroluminescence, excited fluorescence, photochromism, nonlinear optical chromophores, transistors with high mobilities of on/off ratios, charge-transfer complexes and labeling for biological systems.

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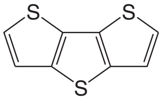
Among the six isomers, dithieno[3,2-*b*;2′,3′-*d*] **1** is the most studied one as the orientation of the fused three thiophene rings leads to a better conjugation. Considering its suitability for constructing π-conjugated systems, various synthetic methods have appeared in the literature (*1*, *2*), including the method developed by our group (*6*), which led to the development of some interesting materials (*7–10*). It involves ring closure reactions of thiophenes containing 3-mono or 3,4-diketones to form thiophenes or dithiins with the use of Lawesson's reagent (*11*) or phosphorus decasulfide (P_4S_{10}) (*12*). In this study, as a continuation of our research line, the ring closure reaction was performed on thiophene containing 2,5-diketone **5** to obtain 3,4-diaryldithieno[2,3-*b*;3′,2′-*d*]thiophenes (DTT) **2**.



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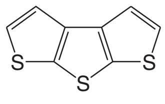
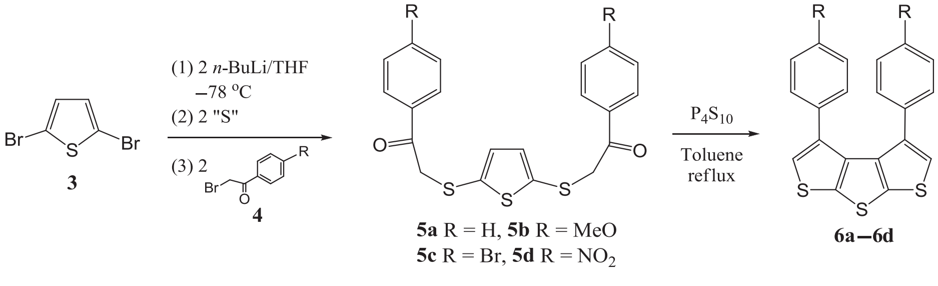


2

2. Results and discussion

2.1. *Syntheses*

Syntheses of DTT **6a–6d** were achieved applying the previously developed ring closure reaction of 1,8-diketone (*6*). Treatment of 2,5-dibromothiophene **3** with two moles of *n*-BuLi at −78°C was followed by addition of two moles of elemental sufur and then two moles of desired α-bromoketone **4** to obtain the corresponding 2,5-diketones **5a–5d** (Scheme 1). The ring closure reaction of **5** was performed using P_4S_{10} (*12*) in refluxing toluene to obtain the DTTs **6a–6d** between 10% and 16%. It is important to note that when an impure P_4S_{10} was used no product was obtained. The easiest way of identifying pure and impure P_4S_{10} is that while the impure P_4S_{10} has yellow color and bad smell, the pure one has very light yellow color and almost none or very slight smell. However, the lower yields of the DTTs **2** is not related to the purity of P_4S_{10}, as the same P_4S_{10} was used for the syntheses of the DTTs **1** (dithieno[2,3-*b*;2′,3′-*d*]thiophenes), which gave higher yields up to 95% (*8*). It is known that carbons 3- and 4- of a thiophene ring are less nucleophile compare with the carbons 2- and 5-, which could be the possible explanation for the lower yields of the ring closure reactions of **5a–5d**.



Scheme 1. Syntheses of the DTTs **6a–6d**.

2.2. *Electrochemistry*

The oxidation reduction behaviors of the monomers **6a–6d** were investigated by cyclic voltammetry (CV). The voltammograms were recorded in acetonitrile/tetrabutylammonium

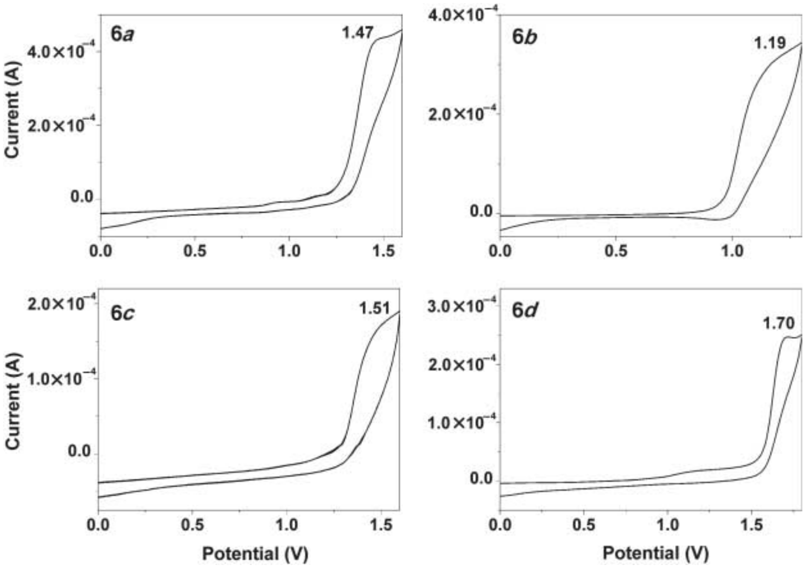


Figure 1. Cyclic voltammograms of DTTs. 1×10^{-3} M solutions of **6a–6d** in acetonitrile, 0.1 M Bu_4NPF_6; 100 mV/s scan rate, Pt wires as working and counter electrodes and Ag/AgCl as a reference electrode.

hexafluorophosphate (0.1 M) solvent-electrolyte couple, using a CV cell consisting of Pt wire as working and counter electrodes and Ag/AgCl as a reference electrode. Solutions were prepared as 1×10^{-3} M, monomer concentrations and the experiments were conducted at room temperature.

The monomers **6a–6c**, having R groups "H," "MeO," "Br" and "NO_2," respectively, displayed oxidation potentials between 1.19 and 1.70 V (Figure 1). Regarding the nature of the "R" groups on the phenyl moiety, the oxidation potentials followed the order of **6d** (1.70 V) > **6c** (1.51 V) > **6a** (1.47 V) > **6b** (1.19 V). While the DTT **6d**, having strong electron withdrawing nitro group had the highest oxidation potential, the DTT **6b**, having strong electron donating methoxy group had the lowest oxidation potential. As a next step, their electropolymerizations were attempted. However, in spite of all the efforts, including different scan rates, altering the solvent-electrolyte couple, applying constant potential, etc., it was not successful. Rather than obtaining an increase at wave intensities of the CV curves, a decrease was obtained (Figure 2). In order to understand the behaviors of the monomers during the electropolymerization, a computational study was conducted.

2.3. *Computational study*

Geometry optimizations of the symmetric DTT molecules were performed within C_2 symmetry constraints at the DFT level, using the Gaussian 03 program (*13*). While the hybrid DFT method B3LYP (*14*) with a conventional all-electron basis set 6-31+G(d) was applied on closed shell molecules, the radical cations were located at unrestricted B3LYP/6-31 + G(d) level. The minima were verified by analyzing the harmonic vibrational frequencies, using analytical second derivatives, which have NIMAG = 0. Single point calculations, including solvent effects at UB3LYP/6-311++G(d,p) level, were conducted on gas phase optimized geometries to obtain spin densities. Solvent effects were incorporated by using self-consistent reaction field with a united atom Hartree–Fock parametrization (*15*) of the polarizable continuum model (*16*) as implemented in Gaussian 03 package. Acetonitrile ($\varepsilon = 36.64$) was employed as a solvent to mimic the measurement and electro-polymerization conditions. The spin densities were visualized, using GaussView 5.0 (Figure 3).

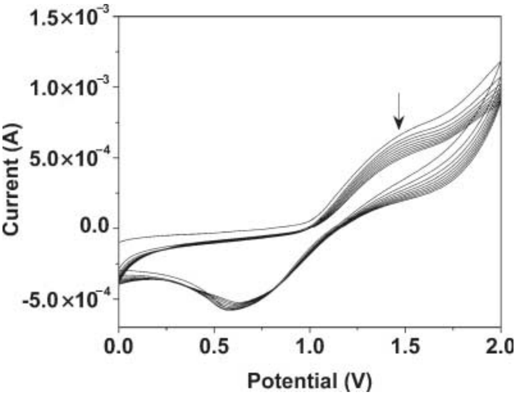


Figure 2. Electropolymerization study of **6a**. 1×10^{-3} M solution of **6a** in acetonitrile, 0.1 M Bu_4NPF_6; 100 mV/s scan rate, Pt wires as working and counter electrodes and Ag wire as a reference electrode.

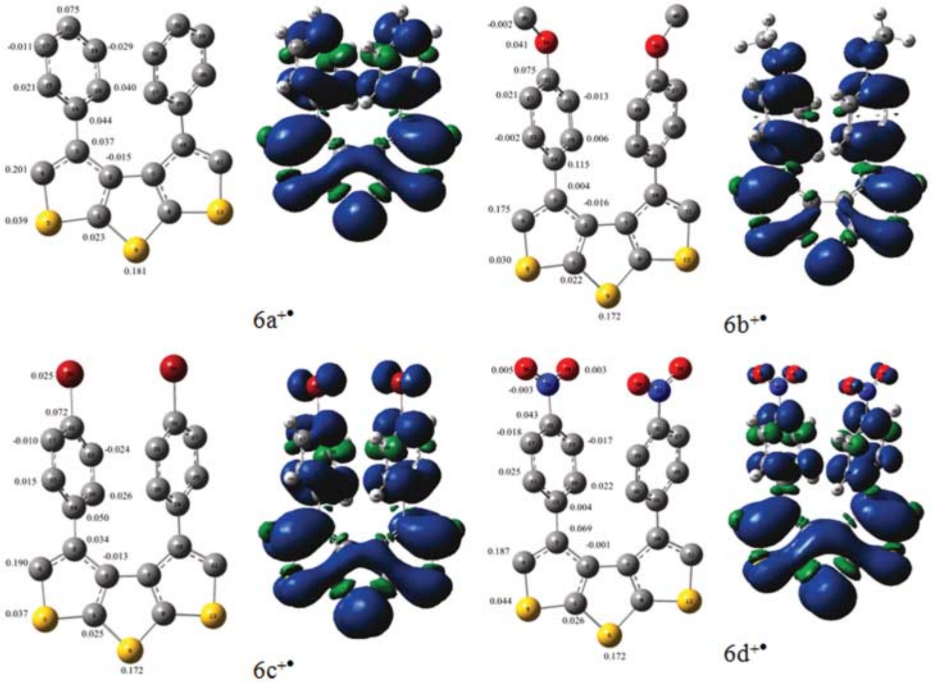


Figure 3. Spin densities and the spin surfaces of the radical cations of **6a–6d**.

Computational results indicated that the DTT **6a**, having spin densities of 0.20 on thiophene α-carbons (**4** and **11**), looked the best candidate for an electro-polymerization. Replacing the hydrogen atom at the *para* position of the phenyl ring with Br, NO_2 and MeO reduced the spin densities slightly to 0.190, 0.187 and 0.175, respectively. Although the computational studies demonstrated that the DTTs had potential for electropolymerization, all the attempts for **6a–6d** were failed. Then, the computational study was extended to the corresponding dimers of the monomers. UB3LYP/6-31+G(d) level optimization with C_2 symmetry constrain revealed the fact that the dimer is not undergoing further polymerization due to the zero spin densities at the corresponding carbon atoms (**10** and **38**) (Figure 4). When the dimer is closely examined, accumulation of electron density through the atoms 1-4-45-42 could easily be observed. This

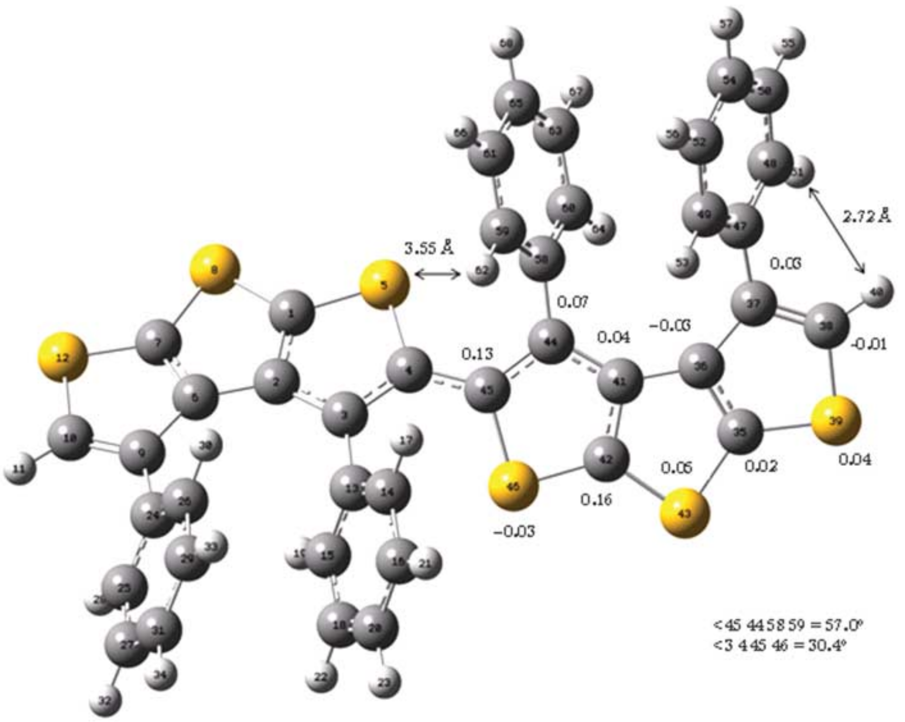


Figure 4. Spin densities of the radical cation of the dimer.

explains that while the two thiophenes, connecting the DTTs, have a good deal of conjugation, it cannot be extended to the other thiophenes as the thiophenes in the middle of each DTT break the conjugation. Expected steric hindrance, emerging from the interaction of the closest hydrogen atoms **51** located at the *ortho* position of the phenyl unit and **40**, proximate to the sulphur atom **39**, could also affect the polymerization, owing to the short distance of 2.72 Å (*17*). According to the reported C–H· · · S hydrogen bond distance of ∼2.7 Å (*18*), predicted distance of 3.55 Å between sulphur (**5**) and hydrogen (**62**) is too long and points out the absence of hydrogen bonding. Moreover, Van der Waals interactions (∼3.0 Å) cannot be observed (*19*).

3. Conclusion

3,4-Diaryl substituted DTT were synthesized, applying the diketone ring closure reaction, using P_4S_{10}. All attempts for their electrochemical polymerizations were failed. Computational chemistry studies revealed that although the DTTs had enough spin densities for electropolymerization at carbon 2- of the peripheral thiophenes, their dimers had spin densities less than zero, which prevented further chain elongation leading to their polymers.

4. Experimental

4.1. *General*

2,5-dibromothiophene (Across) phosphorus decasulfide, 2-bromoacetophenone, 2-bromo-4′-methoxyacetophenone, 2-bromo-4′-nitroacetophenone, 2,4′-dibromoacetophenone, *t*-butyllithium, dichloromethane (Aldrich), diethyl ether, toluene and sodium bicarbonate (Merck) were used without further purification except for diethyl ether, which was dried over metallic sodium. CH-Instruments Model 400A was used as a potentiostat for the CV studies. Fourier Transform Infrared Spectrometer (FTIR) spectra were recorded on a Thermo Nicolet 6700 FT–IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian model NMR (500 MHz). Proton and carbon chemical shifts are reported in ppm downfield from tetramethylsilane. Mass spectra were recorded on Thermo LCQ-Deca ion trap mass instruments.

4.2. *2,2′-(Thiophene-2,5-diylbis(sulfanediyl))bis(1-phenylethanone) 5a*

To a solution of 2,5-dibromothiophene (5.4 mmol, 1.3 g), dissolved in dry diethyl ether (50 ml), was added *tert*-butyllithium (5.9 mmol, 3.1 ml, 1.9 M) at −78°C under nitrogen atmosphere, and the mixture was stirred for 1 h at the same temperature. Then, S_8 (5.4 mmol, 0.173 g) was added and the mixture was stirred for 1 h. This process was repeated with the same quantities of *tert*-butyllithium and S_8 in the same conditions. The mixture was placed into an ice bath and 2-bromoacetophenone (10.8 mmol, 2.1 g) was added portion wise. Stirring was continued overnight at room temperature under nitrogen atmosphere. The reaction was quenched with water (10 ml). The solution was extracted with dichloromethane and the organic layer was dried over Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The crude product was separated by column chromatography eluting with *n*-hexane/CH_2Cl_2: 3/1 to give the title compound **5a** (0.73 g, 35%) as a light yellow powder, mp 75–77°C. IR (Attenuated Total Reflectance (ATR), diamond) 3084, 3060, 2948, 2904, 1906, 1814, 1673, 1595, 1578, 1498, 1404, 1319, 1182, 1159, 1075, 1012, 964, 882, 749, 686, 521 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.90 (dd, $J = 7.4$ Hz, 1.2 Hz, 4H), 7.58 (dt, $J = 7.4$ Hz, 1.2 Hz, 2H), 7.46 (t, $J = 7.4$ Hz, 4H), 6.95 (s, 2H), 4.19 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 193.6, 136.9, 135.3, 135.1, 133.6, 128.7, 128.6, 45.1; APCIMS: $m/z = 385$ ($M^+ + 1$); Anal. Calcd. for $C_{20}H_{16}O_2S_3$(384): C, 62.44; H, 4.19%; found: C, 62.02; H, 4.25%.

The following were similarly prepared.

4.3. *2,2′-(Thiophene-2,5-diylbis(sulfanediyl))bis(1-(4-methoxyphenyl)ethanone) 5b*

The crude product was separated by column chromatography eluting with *n*-hexane/CH_2Cl_2: 2/1 to give the title compound **5b** (0.558 g, 21%) as a light brown solid, mp 76–77°C. IR (ATR, diamond) 3075, 3004, 2965, 2934, 2838, 1669, 1597, 1573, 1509, 1420, 1310, 1282, 1170, 1026, 993, 829, 772, 602, 557 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.87 (d, $J = 8.4$ Hz, 4H), 6.94 (s, 2H), 6.33 (d, $J = 8.4$ Hz, 4H), 4.14 (s, 4H), 3.87 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 192.3, 163.8, 137.0, 134.9, 130.0, 128.3, 113.9, 55.5, 44.8; APCIMS: $m/z = 445$ ($M^+ + 1$); Anal. Calcd. for $C_{22}H_{20}O_4S_3$ (444): C, 59.43; H, 4.50%; found: C, 59.55; H, 4.68%.

4.4. *2,2′-(Thiophene-2,5-diylbis(sulfanediyl))bis(1-(4-bromophenyl)ethanone) 5c*

The crude product was separated by column chromatography eluting with *n*-hexane/CH_2Cl_2: 3/1 to give the title compound **5c** (1 g, 31%) as a light brown powder, mp 104–106°C. IR (ATR, diamond) 3099, 3056, 2935, 2897, 1922, 1666, 1582, 1482, 1396, 1288, 1191, 1102, 1008, 992, 809, 795, 667, 562, 488 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.76 (d, $J = 8.6$ Hz, 4H), 7.61 (d, $J = 8.6$ Hz, 4H), 6.92 (s, 2H), 4.12 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 192.6, 136.7, 135.4, 133.9, 132.1, 130.1, 128.9, 44.7; APCIMS: $m/z = 543$ ($M^+ + 1$); Anal. Calcd. for $C_{20}H_{14}O_2S_3$ (542): C, 44.30; H, 2.59%; found: C, 43.63; H, 2.72%.

4.5. *2,2′-(Thiophene-2,5-diylbis(sulfanediyl))bis(1-(4-nitrophenyl)ethanone) 5d*

The crude product was separated by column chromatography eluting with *n*-hexane/CH_2Cl_2: 2/1 to give the title compound **5d** (0.84 g, 26%) as a brown powder, mp 162–165°C. IR (ATR, diamond) 3357, 3109, 3075, 2918, 2860, 2781, 2701, 2451, 2290, 1681, 1602, 1514, 1342, 1268, 1185, 1110, 998, 853, 758, 683, 541, 435 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.30 (d, $J = 9.0$ Hz, 4H), 7.90 (d, $J = 9.0$, 4H), 7.03 (s, 2H), 4.15 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 194.6, 153.2, 142.3, 139.1, 138.5, 132.4, 126.6, 47.2; APCIMS: $m/z = 474$ (M^+); Anal. Calcd. for $C_{20}H_{14}N_2O_6S_3$ (474): C, 50.60; H, 2.96%; found: C, 50.95; H, 2.63%.

4.6. *3,4-Bisphenyldithieno[2,3-b;3′,2′-d]thiophene 6a*

A mixture of P_4S_{10} (1 g, 2.25 mmol) and **5a** (0.29 g, 0.75 mmol) was refluxed in toluene (70 ml) for 4 h. The mixture was then extracted with dichloromethane and water. The organic layer was dried over Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The crude product was separated by column chromatography eluting with hexane/CH_2Cl_2: 8/1 to give the title compound **6a** (26 mg, 10%) as a yellow powder, mp 108–109°C. IR (ATR, diamond) 3024, 2957, 2920, 2850, 1938, 1884, 1678, 1596, 1540, 1486, 1443, 1369, 1327, 1275, 1206, 1183, 1156, 1076, 1029, 903, 804, 748, 687 cm^{-1}; 1H NMR (500 MHz, CDC13) δ (ppm) 7.64 (d, $J = 8.0$ Hz, 4H), 7.39 (t, $J = 8.0$ Hz, 4H), 7.29 (m, 4H); 13C NMR (125 MHz, CDC13) δ (ppm) 143.6, 134.3, 128.8, 127.5, 125.6, 123.9; APCIMS: $m/z = 348$ (M^+); Anal. Calcd. for $C_{20}H_{12}S_3$ (348): C, 69.90; H, 3.46%; found: C, 69.58; H, 3.72%.

The following were similarly prepared.

4.7. *3,4-Bis(4′-methoxyphenyl)dithieno[2,3-b;3′,2′-d]thiophene 6b*

The crude product was separated by column chromatography eluting with *n*-hexane/CH_2Cl_2: 6/1 to give the title compound **6b** (38 mg, 12%) as a yellow powder, mp 126–128°C. IR (ATR, diamond) 3090, 2997, 2956, 2834, 1891, 1673, 1604, 1519, 1501, 1456, 1291, 1174, 1026, 827, 795, 575 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.23 (s, 2H), 7.12 (d, $J = 8.7$ Hz, 4H), 6.80 (d, $J = 8.7$, 4H), 3.79 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 158.5, 141.3, 130.1, 129.1, 126.8, 123.0, 114.2, 113.5, 55.2; APCIMS: $m/z = 409$ ($M^+ + 1$); Anal. Calcd. for $C_{22}H_{16}O_2S_3$ (408): C, 64.66; H, 3.96%; found: C, 64.20; H, 4.28%.

4.8. *3,4-Bis(4′-bromophenyl)dithieno[2,3-b;3′,2′-d]thiophene 6c*

The crude product was separated by column chromatography eluting with *n*-hexane/CH_2Cl_2: 6/1 to give the title compound **6c** (28 mg, 16%) as a yellow powder, mp 193–195°C. IR (ATR, diamond) 3077, 3037, 3018, 2970, 1902, 1770, 1650, 1587, 1555, 1479, 1447, 1333, 1273, 1207, 1117, 1103, 1006, 935, 825, 794, 627, 560, 466 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.51 (d, $J = 8.8$ Hz, 4H), 7.48 (d, $J = 8.8$ Hz, 4H), 7.27 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 142.7, 133.0, 132.0, 127.0, 124.5, 122.6, 121.5; APCIMS: $m/z = 507$ ($M^+ + 1$); Anal. Calcd. for $C_{20}H_{10}Br_2S_3$ (506): C, 47.46; H, 1.98%; found: C, 47.14; H, 2.46%.

4.9. *3,4-Bis(4′-nitrophenyl)dithieno[2,3-b;3′,2′-d]thiophene 6d*

The crude product was separated by column chromatography eluting with *n*-hexane/CH_2Cl_2: 8/1 to give the title compound **6d** (24 mg, 14%) as a yellow powder, mp 195–197°C. IR (ATR, diamond) 3077, 3037, 3018, 2970, 1902, 1770, 1650, 1587, 1479, 1447, 1333, 1273, 1117, 1075, 1006, 935, 825, 794, 627, 560, 466 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.51 (d, $J = 8.8$ Hz, 4H), 7.48 (d, $J = 8.8$ Hz, 4H), 7.27 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 152.9, 146.9, 135.5, 129.8, 126.0, 124.5, 124.3, 111.5; APCIMS: $m/z = 439$ ($M^+ + 1$); Anal. Calcd. for $C_{20}H_{10}N_2O_4S_3$ (438): C, 54.77; H, 2.30%; found: C, 54.12; H, 2.78%.

Acknowledgements

We thank Istanbul Technical University, Turkey, for a grant to Sule Taskiran Cankaya (Ph.D.), National Center for High Performance Computing (UYBHM) for the computer time provided (d0001), Unsped Global Logistic for financial support and TUBITAK for a Fellowship (2216) to Dr M. Emin Cinar.

References

(1) Ozturk, T.; Ertas, E.; Mert, O. *Tetrahedron* **2005,** *61,* 11055–11077.

(2) Skabara, P.J. In *Handbook of Thiophene-Based Materials*; Perepichka, I.F., Perepichka, D.F., Eds.; John Wiley & Sons: Chichester, 2009; Chapter 3.

(3) Forrest, S.R.; Thompson, M.E. (Guest eds.). *Chem. Rev.* **2007,** *107,* 923–1386.

(4) Tang, C.W.; van Slyke, S.A. *Appl. Phys. Lett.* **1987,** *51,* 913–915.

(5) Dimitrakopoulos, C.D.; Malenfant, P.R.L. *Adv. Mater.* **2002,** *14,* 99–117.

(6) Ertas, E.; Ozturk, T. *Tetrahedron Lett.* **2004,** *45,* 3405–3407.

(7) Capan, A.; Veisi, H.; Goren, A.C.; Ozturk, T. *Macromolecules.* **2012,** *45,* 8228–8236.

(8) Osken, I.; Sahin, O.; Gundogan, A.S.; Bildirir, H.; Capan, A.; Ertas, E.; Eroglu, M.S.; Wallis, J.D.; Topal, K.; Ozturk, T. *Tetrahedron* **2012,** *68,* 1216–1222.

(9) Osken, I.; Bildirir, H.; Ozturk, T. *Thin Solid Films* **2011,** *519,* 7707–7711.

(10) Dundar, P.; Osken, I.; Sahin, O.; Ozturk, T. *Synth. Met.* **2012,** *162,* 1010–1015.

(11) Ozturk, T.; Ertas, E.; Mert, O. *Chem. Rev.* **2007,** *107,* 5210–5278.

(12) Ozturk, T.; Ertas, E.; Mert, O. *Chem. Rev.* **2010,** *110,* 3419–3478.

(13) Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Montgomery, J.A.; Vreven, T., Jr.; Kudin, K.N.; Burant, J.C.; Millam, J.M.; Iyengar, S.S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G.A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J.E.; Hratchian, H.P.; Cross, J.B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Ayala, P.Y.; Morokuma, K.; Voth, G.A.; Salvador, P.; Dannenberg, J.J.; Zakrzewski, V.G.; Dapprich, S.; Daniels, A.D.; Strain, M.C.; Farkas, O.; Malick, D.K.; Rabuck, A.D.; Raghavachari, K.; Foresman, J.B.; Ortiz, J.V.; Cui, Q.; Baboul, A.G.; Clifford, S.; Cioslowski, J.; Stefanov, B.B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R.L.; Fox, D.J.; Keith, T.; Al-Laham, M.A.; Peng, C.Y.; Nanayakkara, A.; Challacombe, M.; Gill, P.M.W.; Johnson, B.; Chen, W.; Wong, M.W.; Gonzalez, C.; Pople, J.A. *Gaussian 03*; Gaussian, Inc.: Wallingford, CT, 2004.

(14) (a) Becke, A.D. *J. Chem. Phys.* **1993,** *98,* 1372–1377. (b) Becke, A.D. *J. Chem. Phys.* **1993,** *98,* 5648–5652. (c) Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev. B.* **1988,** *37,* 785–789.

(15) Barone, V.; Cossi, M.; Tomasi, J. *J. Chem. Phys.* **1997,** *107,* 3210–3221.

(16) (a) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981,** *55,* 117–129; (b) Cammi, R.; Tomasi, J. *J. Comput. Chem.* **1995,** *16,* 1449–1458; (c) Barone, V.; Cossi, M.; Tomasi, J. *J. Comput. Chem.* **1998,** *19,* 404–417.

(17) Ando, S.; Ueda, M. *Synth. Met.* **2002,** *129,* 207–213.

(18) Esparza-Ruiz, A.; Pena-Hueso, A.; Hernandez-Diaz, J.; Flores-Parra, A.; Contreras, R. *Cryst. Growth Des.* **2007,** *7,* 2031–2040.

(19) Smith, W.B.; Harris, M.C. *J. Org. Chem.* **1980,** *45,* 355–356.