ORGANIC LETTERS

2004
Vol. 6, No. 2
273−276

Planarized Star-Shaped Oligothiophenes with Enhanced π-Electron Delocalization

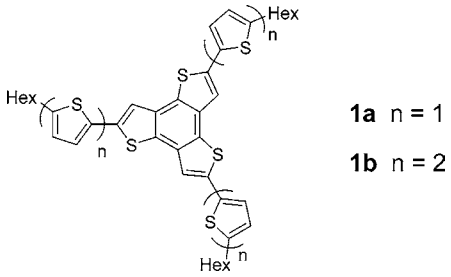
Yohann Nicolas, Philippe Blanchard,* Eric Levillain, Magali Allain,[†] Nicolas Mercier,[†] and Jean Roncali*

Groupe Systèmes Conjugués Linéaires, IMMO, UMR CNRS 6501, Université d'Angers, 2 Bd Lavoisier, F-49045 Angers, France, and IMMO, UMR CNRS 6501, Université d'Angers, 2 Bd Lavoisier, F-49045 Angers, France

philippe.blanchard@univ-angers.fr; jean.roncali@univ-angers.fr

Received November 21, 2003

ABSTRACT



1a n = 1

1b n = 2

Planarized star-shaped oligothiophenes 1 have been synthesized by connecting short-chain oligothiophenes on a benzo[1,2-*b*:3,4-*b*′:5,6-*b*′′]-trithiophene central core. Their electrochemical and optical properties have been characterized by cyclic voltammetry and UV−visible spectroscopy, respectively. These results associated with theoretical calculations show the advantage of benzotrithiophene as a central core in terms of π-electron delocalization.

Thiophene-based π-conjugated oligomers[1] are the subject of considerable current interest due to their use as organic semiconductors for the realization of devices such as field-effect transistors,[2] light-emitting diodes,[3] and photovoltaic cells.[4]

Despite the huge amount of work already invested in these various applications, it is clear that further progress in these fields implies an intensification of the research effort focused on the design and synthesis of new compounds with electrochemical, optical, and electronic properties specifically tailored for each type of application.

In this context, we report here the synthesis and preliminary characterizations of the first members of a new series of star-shaped oligothiophenes in which three short linear oligothiophene chains are connected to a central rigid trithienobenzene core.

Star-shaped oligothiophenes with three or more oligothiophene chains attached to a central benzenic core have already been reported by several groups.[5] However, as shown by molecular models and confirmed by experimental data,

[†] IMMO.

(1) Bäuerle, P. In *Electronic Materials: The Oligomer Approach*; Müllen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, 1998; Chapter 2, pp 105−197.

(2) (a) Dimitrakopoulos, C. D.; Malenfant, P. *Adv. Mater*. **2002**, *14*, 99−117. (b) Katz, H. E.; Lovinger, A. J.; Laquindanum, J. G. *Chem. Mater*. **1998**, *10*, 457−459. (c) Garnier, F.; Yassar, A.; Hajlaoui, R.; Horowitz, G.; Deloffre, F.; Servet, B.; Ries, S.; Alnot, P. *J. Am. Chem. Soc*. **1993**, *115*, 8716−8721. (d) Garnier, F.; Hajlaoui, R.; El Kassmi, A.; Horowitz, Laigre, L.; Porzio, W.; Armanini, M.; Provasoli, F. *Chem. Mater*. **1998**, *10*, 3334−3339.

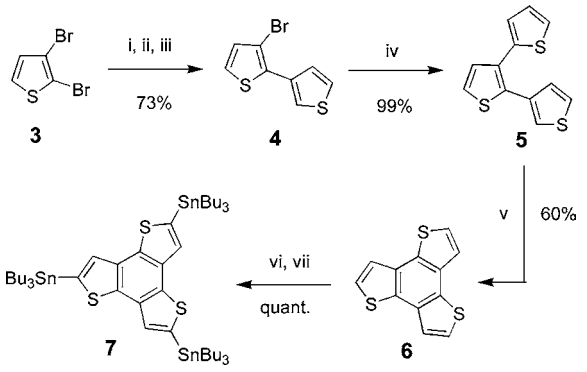
(3) (a) Mitschke, U.; Bäuerle, P. *J. Mater. Chem*. **2000**, *10*, 1471−1507.

(4) (a) Videlot, C.; El Kassmi, A.; Fichou, D. *Solar Energy Mater. Solar Cells* **2000**, *63*, 69. (b) Fichou, D. *J. Mater. Chem*. **2000**, *10*, 571−588. (c) Noma, N.; Tsuzuki, T.; Shirota, Y. *Adv. Mater*. **1995**, *7*, 647−648.

(5) (a) Chérioux, F.; Guyard, L.; Audebert, P. *Chem. Commun*. **1998**, 2225−2226. (b) Kotha, S.; Chakraborty, K.; Brahmachary, E. *Synlett* **1999**, 10, 1621−1623. (c) Bras, J.; Guillerez, S.; Pépin-Donat, B. *Chem. Mater*. **2000**, *12*, 2372−2384. (d) Chérioux, F.; Guyard, L. *Adv. Funct. Mater*. **2001**, *11*, 305−309. (e) Geng, Y.; Fechtenkötter, A.; Müllen, K. *J. Mater. Chem*. **2001**, *11*, 1634−1641. (f) Pappenfus, T. M.; Mann, K. R. *Org. Lett*. **2002**, *4*, 3043−3046. (g) Ponomarenko, S. A.; Kirchmeyer, S.; Elschner, A.; Huisman, B.-H.; Karbach, A.; Drechsler, D. *Adv. Funct. Mater*. **2003**, *13*, 591−596. (h) Inoue, S.; Nischiguchi, S.; Murakami, S.; Aso, Y.; Otsubo, T.; Vill, V.; Mori, A.; Ujiie, S. *J. Chem. Res., Synop*. **1999**, 596−597.

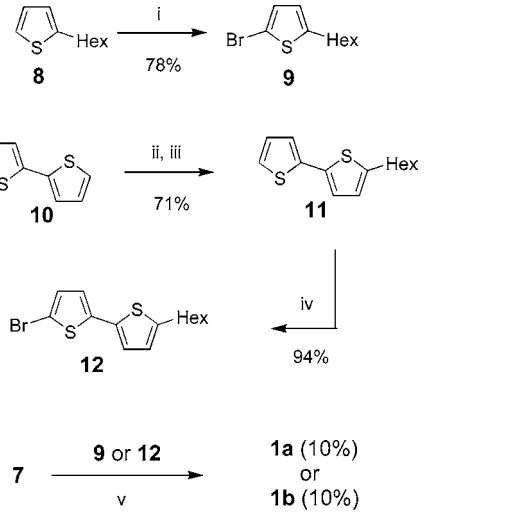
10.1021/ol0362764 CCC: $27.50
Published on Web 12/19/2003

Scheme 1. Synthesis of Trithienobenzene Derivatives[a]



[a] Reagents and conditions: (i) *n*-BuLi (1 equiv), THF, −70 °C; (ii) tetrahydrothiophene-3-one, THF, −70 °C to reflux, then aq HCl; (iii) chloranil, ethyleneglycol, reflux; (iv) 2-thienylmagnesium bromide, NidpppCl$_2$, Et$_2$O, reflux; (v) *hν*, cat. I$_2$, O$_2$, toluene; (vi) *n*-BuLi (6 equiv), THF, 0 °C and then 20 °C; (vii) Bu$_3$SnCl.

Scheme 2. Synthesis of Star-Shaped Molecules **1**[a]



[a] Reagents and conditions: (i) NBS (1.05 equiv), DMF, −20 °C; (ii) C$_5$H$_{11}$COCl, SnCl$_4$, benzene, 0 °C; (iii) LiAlH$_4$, AlCl$_3$, Et$_2$0, 20 °C; (iv) NBS (1.05 equiv), DMF, 20 °C; (v) cat. Pd(PPh$_3$)$_4$, toluene, reflux.

the steric interactions associated with the grafting of a thiophene moiety on a benzene ring produce a dihedral angle that results in a limitation of the effective conjugation.[5a−d,g]

To solve this problem we describe here the use of a rigid and planar central core involving three thiophene rings fused to the benzenic ring with the aim of building a planar conjugated molecule of C_{3h} symmetry.

As generally observed in the oligothiophene series,[6] the dihedral angle between two consecutive thiophene rings is close to 0° in the solid state. Therefore, the trithienobenzene core offers the possibility of building planar star-shaped oligothiophenes with enhanced π-electron delocalization.

The target compounds **1** have been synthesized according to the procedure depicted in Schemes 1 and 2. Commercially available 2,3-dibromothiophene **3** was subjected to a regioselective lithium−bromine exchange at the 2-position of the thiophene ring using 1 equiv of *n*-BuLi at low temperature. After reaction of this lithium salt with tetrahydrothiophene-3-one and subsequent acidification, the resulting carbinol was directly dehydrated and oxidized in the presence of chloranil in refluxing ethylene glycol to afford bithiophene **4** in good yield.[7] A nickel-catalyzed Kumada coupling reaction between compound **4** and freshly prepared 2-thienylmagnesium bromide gave terthiophene **5** in excellent yield.[8] The shamrock-shaped key central core benzo[1,2-*b*:3,4-*b*′:5,6-*b*″]trithiophene **6** was then prepared by oxidative photocyclization by irradiation of a diluted toluene solution of **5** under aerobic conditions in the presence of a catalytic amount of iodine.

A modification of the literature procedure[9] by using a 400 W high-pressure Hg lamp allowed shortening of the irradiation time from 11 to 2 h and improvement of the reaction yield from 34 to 60%.[10] This reaction appeared to be highly regioselective since only one regioisomer was obtained. The presence of only two doublets at 7.54 and 7.64 ppm, reflecting a high degree of molecular symmetry and the typical value of the thiophenic α,*β*-coupling constant (^3J = 5.4 Hz) observed in the ^{1}H NMR spectrum, are in good agreement with the structure of **6**.

Single crystals, grown by slow evaporation of a solution of **6** in a chloroform/ethanol mixture, have been analyzed by X-ray diffraction. The obtained crystallographic structure definitely confirms the regular head-to-tail orientation of the thiophene rings and the expected fully planar geometry of molecule **6** (Figure 1).

Regioselective lithiation of compound **6** at the α-position of each thiophene ring with 6 equiv of *n*-BuLi and subsequent quenching with tributylstannyl chloride gave the corresponding tristannyl reagent **7**.

2-Bromo-5-hexylthiophene **9** and 5-bromo-5′-hexyl-2,2′-bithiophene **12** were prepared by treatment of 2-hexylthiophene **8** and 5-*n*-hexyl-2,2′-bithiophene **11**, respectively, with NBS in *N*,*N*-dimethylformamide[11] (Scheme 2). Compound **11** was preferably synthesized by successive acylation and reduction from 2,2′-bithiophene **10** in order to circumvent the difficulties associated with the purification of **11** when prepared by direct alkylation of the lithium salt of 2,2′-bithiophene.[12]

(6) (a) van Bolhuis, F.; Wynberg, H.; Havinga, E. E.; Meijer, E. W.; Staring, E. G. J. *Synth. Met.* **1989**, *30*, 381. (b) Chaloner, P. A.; Gunatunga, S. R.; Hitchcock P. B. *Acta Crystallogr., Sect. C* **1994**, *50*, 1941. (c) Pelletier, M.; Brisse, F. *Acta Crystallogr., Sect. C* **1994**, *50*, 1942.

(7) Wynberg, H.; Heeres, G. J.; Jordens, P.; Sinnige, H. J. M. *Recl. Trav. Chim.* **1970**, *89*, 545−552.

(8) Jayasuriya, N.; Kagan, J. *Heterocycles* **1986**, *24*, 2901−2904.

(9) Jayasuriya, N.; Kagan, J. *J. Org. Chem.* **1989**, *54*, 4203−4205.

(10) A previous route to compound **6** involving more drastic conditions has been reported: Proetzsch, R.; Bieniek, D.; Korte, F. *Tetrahedron Lett.* **1972**, *6*, 543−544.

(11) Bäuerle, P.; Würthner, F.; Götz, G.; Effenberger, F. *Synthesis* **1993**, 1099−1103.

(12) Improved purification of **11** was recently reported by: Sotgiu, G.; Zambianchi, M.; Barbarella, G.; Botta, C. *Tetrahedron* **2002**, *58*, 2245−2251.

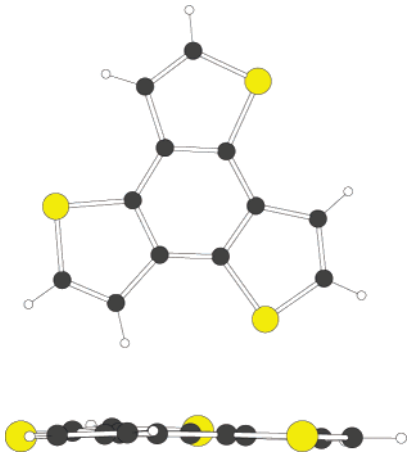


Figure 1. Crystallographic structure of compound **6**.

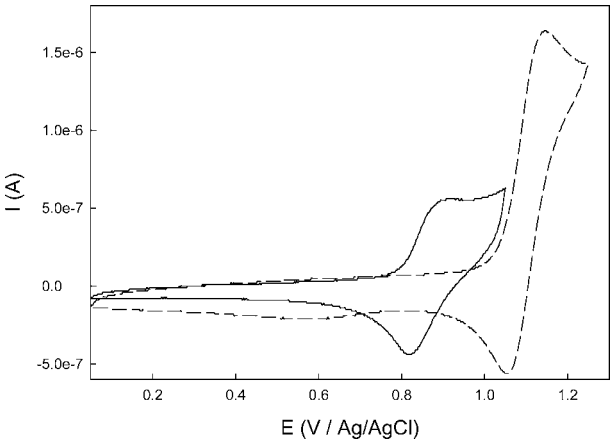
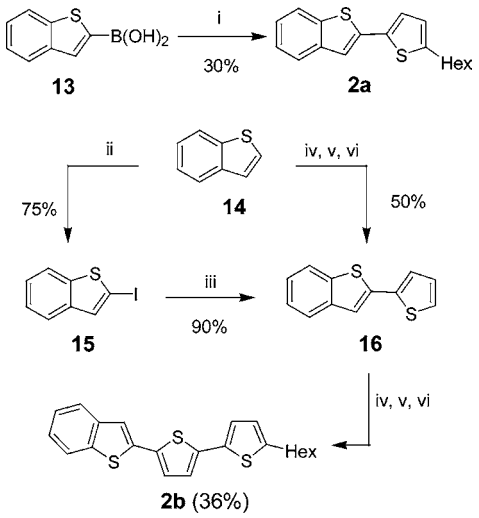


Figure 2. Cyclic voltammograms of 0.5 mM solutions of **1b** (solid line) and **2b** (dashed line,) in 0.2 M Bu_4NPF_6/CH_2Cl_2, Pt electrodes, scan rate = 100 mV/s.

The target compounds **1a** and **1b** were then assembled by a threefold Stille reaction between the tris(stannyl) derivative **7** and 2-bromo-5-*n*-hexylthiophene **9** or 5-bromo-5′-*n*-hexyl-2,2′-bithiophene **12**, respectively. Thus, treatment of compound **7** with 4 equiv of bromo derivatives **9** or **12** in the presence of a catalytic amount of $Pd(PPh_3)_4$ led to the formation of the target compounds **1a** and **1b**.

The synthesis of the reference linear compounds **2a** and **2b** is described in Scheme 3. Compound **2a** was prepared by Suzuki coupling between thianaphthene-2-boronic acid **13** and bromo derivative **9**. On the other hand, a regioselective lithiation reaction at the free α-position of the thiophene ring of **16** and subsequent reaction with tributylstannyl chloride led to the corresponding stannyl derivative. This intermediate compound was directly engaged in the final Stille reaction with 2-bromo-5-*n*-hexylthiophene, affording **2b**. Derivative **16** was obtained by a Stille coupling reaction either between 2-iodobenzo[*b*]thiophene **15** and 2-tributylstannylthiophene or between the stannyl derivative of thianaphthene **14** and 2-bromothiophene.

Scheme 3. Synthesis of the Linear Molecules **2**[a]



[a] Reagents and conditions: (i) **9** (1.1 equiv), DME, $Pd(PPh_3)_4$, $Ba(OH)_2$, H_2O, reflux; (ii) *n*-BuLi, THF, −50 °C then I_2, −50 to 20 °C; (iii) 2-tributylstannylthiophene, cat. $Pd(PPh_3)_4$, toluene, reflux; (iv) *n*-BuLi (1 equiv), THF, 0 °C then 20 °C; (v) Bu_3SnCl, 20 °C; (vi) 2-bromothiophene or 2-bromo-5-hexylthiophene, $Pd(PPh_3)_4$, toluene, reflux.

The electronic properties of the star-shaped compounds **1** and of the corresponding linear reference compounds **2** have been analyzed by cyclic voltammetry and UV−vis spectroscopy. The cyclic voltammograms (CV) of **1** and **2** exhibit a one-electron oxidation wave corresponding to the formation of the cation radical. An analysis of the electro-oxidation of compound **1b** by thin-layer cyclic voltammetry using 2,3-dichloro-1,4-naphthoquinone as an internal reference definitively showed that the oxidation process involves only one electron per molecule.

At a scan rate of 100 mV/s, the oxidation process, which is irreversible for **1a** and **2a**, becomes reversible for **1b** and quasi-reversible for **2b**, respectively (Figure 2). An analysis of the scan rate dependence of the CV of compound **2b** shows that full reversibility is reached above 1 V/s. The different behaviors of **1b** and **2b** clearly show that the assembly of the benzo-oligothiophenes in a star-shaped system considerably stabilizes the cation radical. It is also worth noting that the difference in intensity between the voltammograms of **1b** and **2b** at the same concentration (0.50 mM (see Figure 2) or 0.25 mM (not shown)) may be correlated to the difference of the related diffusion coefficients in solution, the larger star-shaped molecule probably exhibiting a lower coefficient.

As shown in Table 1, for both series of compounds, the lengthening of the oligothiophene chain induces a negative shift of the anodic peak potential (E_{pa}) due to the extension of the conjugation length. In addition, comparison of the data for compounds **1** and **2** reveals a significant negative shift of E_{pa} for the star-shaped molecules (140 and 220 mV for

Table 1. Electrochemical, Optical, and Thermal Data for Compounds **1** and **2**

compd	E_{pa}/V[a]	λ_{max}/nm[b]	λ_{max}/eV	T_d/°C[c]
1a	1.16	357	3.47	405
1b	0.93	404	3.07	430
2a	1.30	326	3.80	185
2b	1.15	379	3.27	232
6	1.55	288, 267		

[a] Performed with 0.1 mM of compound in 0.2 M Bu_4NPF_6/CH_2Cl_2, Pt electrodes, Ag/AgCl as a reference, scan rate = 100 mV/s. [b] In CH_2Cl_2. [c] Temperature of decomposition corresponding to 5% weight loss from TGA analysis under N_2 with a heating rate of 10 °C/min.

series **a** and **b**, respectively), indicative of an increase of the HOMO levels for compounds **1**.

On the other hand, UV−vis data show that the passage from a linear to a star-shaped system results in a 25−31 nm bathochromic shift of λ_{max} corresponding to a significant decrease of the HOMO−LUMO energy gap (Table 1).

Comparison of the UV−vis data of **1b** to those of a recently described star-shaped oligothiophene based on a benzenic core, namely, 1,3,5-tris[5-(5″-decyl-2,2′:5′2″-terthienyl)]benzene (λ_{max} = 405 nm)[5g] shows that, while both compounds absorb at the same wavelength, the trithienothiophene core allows an economy of six sp^2 carbon atoms, thus underlining the advantage of the fused central core **6** over a simple benzene ring in terms of π-electron delocalization.

To gain more insight into the relationship between structure and electronic properties, the structure of the parent compound of **1b** without hexyl substituents and that of the 1,3,5-tris[5-(2,2′-dithienyl)]benzene were modelized by theoretical calculations based on the density functional method using Gaussian 98 (see Supporting Information). In both cases, optimization was carried out by imposing an all-anti conformation to the thiophene rings. Comparison of the results obtained for the two systems shows that in addition to the full planarization of the central core, in agreement with the X-ray data, connection to the fused trithienobenzene system results in a decrease of the dihedral angle between the central core and the first thiophene ring from ca. 29 to 11°, thus confirming that the use of **6** as a central core leads to a more planar and hence more conjugated system.

The analysis of the thermal stability of **1a** and **1b** by TGA shows that the star-shaped molecules begin to decompose only above 400 °C, that is, more than 200 °C above the decomposition temperature of their linear analogues.

To summarize, the first members of a new class of star-shaped oligothiophenes have been synthesized. Comparison of the electronic properties of these compounds to those of their linear analogues and other already known star-shaped oligothiophenes shows that the use of a centrally fused trithienobenzene core allows development of a new class of planar star-shaped conjugated systems with enhanced π-electron delocalization.

As a first illustration of the potentialities of these new compounds, we have recently shown that heterojunction solar cells based on vacuum-sublimed thin films of the star-shaped compound **1b** exhibit power conversion efficiencies ca. 20 times larger than those obtained with the cells based on the linear compound **2b**.[13]

Acknowledgment. We thank the SCAS of the University of Angers for analytical characterizations and the city of Angers for financial support for Y. N.

Supporting Information Available: Synthetic procedures, structural characterization for all compounds, and X-ray data for compound **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL0362764

(13) De Bettignies, R.; Nicolas, Y.; Blanchard, P.; Levillain, E.; Nunzi, J.-M.; Roncali, J. *Adv. Mater.* **2003**, *15*, 1939−1943.