Pergamon

Tetrahedron Letters, Vol. 35, No. 23, pp. 3957-3960, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)E0713-8

Synthesis and Properties of α-Oligothiophenes Carrying Three Cofacially Oriented Thiophene Rings through Peri Positions of Naphthalenes

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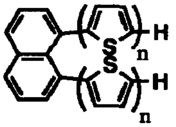
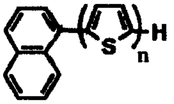
Abstract: 5,5'-Bis[8-(2-thienyl)naphthalene-1-yl]-2,2'-bithiophene and 5,5"-bis[8-(2-thienyl)naphthalene-1-yl]-2,2':5',2"-terthiophene were synthesized starting from 1,8-di(2-thienyl)naphthalene and 5,5'''-bis[8-(5,2'-bithiophene-2-yl)-naphthalene-1-yl]-2,2':5',2":5",2'''-quaterthiophene from 1,8-bis(5,2'-bithiophene-2-yl)naphthalene to investigate intramolecular interactions among the three thiophene units that would be cofacially oriented each other in these molecules.

Oligothiophenes are attractive building blocks for molecular electronic devices. Recently, several molecules which have two perpendicular oligothiophene units bisected through a spiro carbon atom have been synthesized with expectation of obtaining new molecular switches.[1] On the other hand, we have been interested in the molecules that have cofacially oriented α-oligothiophene units in close proximity. In such molecules, two thiophene units would interact with each other to produce additional new interesting physicochemical properties. In this connection, we have investigated the synthesis and properties of naphthalenes (**1a**-**d**) that carry two cofacially oriented α-oligothiophene units at the peri positions.[2] Inspection of ^{1}H and ^{13}C NMR and UV/Vis data of **1a**-**d** and **2a**-**d** including X-ray single crystal structure data of **1b** suggested that the planes of two oligothiophene units of **1a**-**d** are approximately parallel to each other and are at large angles to the plane of naphthalene ring. In accordance with these findings, CV oxidation potential data showed that the radical cations formed from **1a**-**d** were stabilized by intramolecular electron transfer interaction between two oligothiophene units. It is thus expected that increase of the number of stacked oligothiophene layers produces more effective intramolecular polar/π interactions. We report here the synthesis and properties of 5,5'-bis[8-(2-thienyl)naphthalene-1-yl]-2,2'-bithiophene (**3a**), 5,5"-bis[8-(2-thienyl)naphthalene-1-yl]-2,2':5',2"-terthiophene (**3b**), and 5,5'''-bis[8-(5,2'-bithiophene-2-yl)naphthalene-1-yl]-2,2':5',2":5",2'''-quaterthiophene (**3c**) that carry three (oligo)thiophene units which would be cofacially oriented through peri positions of naphthalenes. To our knowledge, synthesis and properties of this type of layered compounds have never been reported.

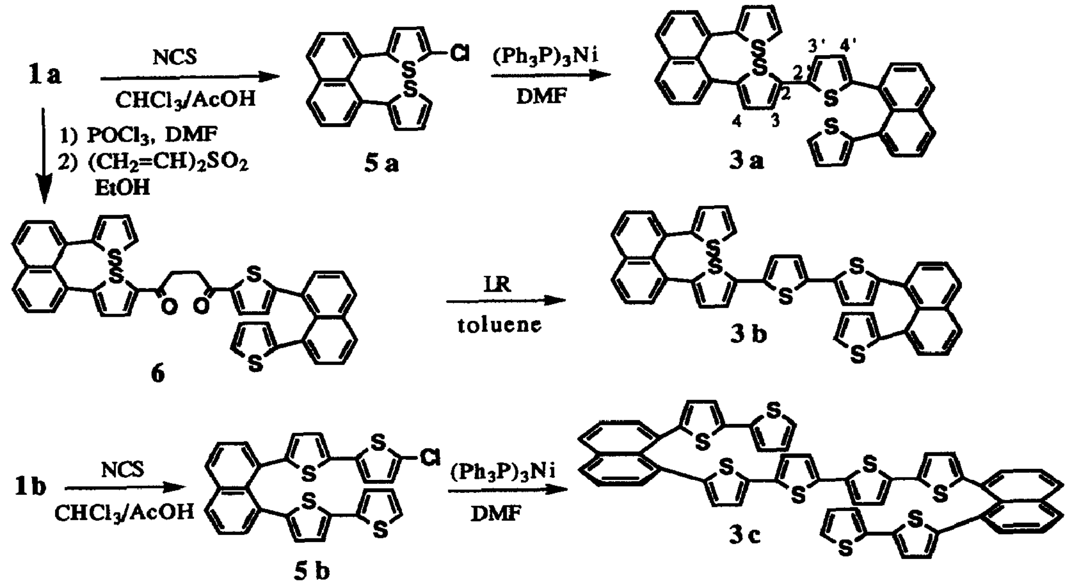


1a: n=1
1b: n=2
1c: n=3
1d: n=4



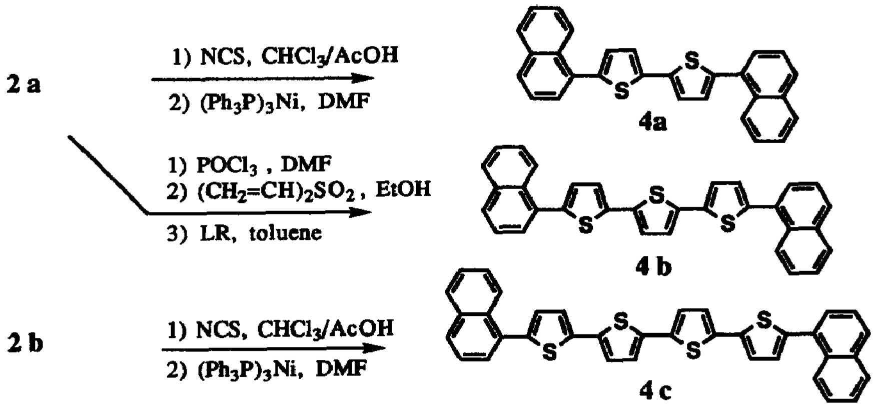
2a: n=1
2b: n=2
2c: n=3
2d: n=4

Chlorination of the 5-position of the thiophene ring of 1,8-di(2-thienyl)naphthalene (**1a**)[2] with 1 equiv. of *N*-chlorosuccinimide (NCS) gave **5a** in 70% yield (Scheme 1). Subsequent self-coupling of **5a** catalyzed by tris(triphenylphosphine)nickel $[(Ph_3P)_3Ni]$[3] gave the desired **3a**[4] in 53% yield. Treatment of **1a** with phosphorus oxychloride in DMF and the coupling of the resulting formyl derivative with divinyl sulfone,[5] which was catalyzed by 3,4-dimethyl-5-(2-hydroxyethyl)thiazolium iodide, gave the corresponding 1,4-diketone **6** in 19% overall yield. The 1,4-diketone **6** was cyclized with Lawesson's reagent[6] in refluxing toluene to give the expected terthiophene **3b**[7] in 64% yield. The $(Ph_3P)_3Ni$-catalyzed self-coupling of **5b**, which was obtained by chlorination of 1,8-bis(5,2'-bithiophene-2-yl)naphthalene (**1b**)[2] with 1 equiv. of NCS in 56% yield, gave the quaterthiophene **3c**[8] as reddish brown powder in 29% yield.



Scheme 1

For comparison with **3a-c**, dinaphthyl-substituted oligothiophenes **4a-c** were synthesized in the manners given in Scheme 2. Every reaction worked cleanly to give **4a-c** in reasonable overall yields.



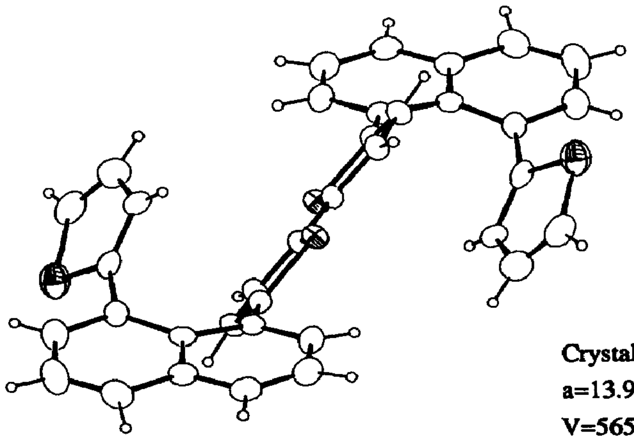
Scheme 2

Both ^{1}H and ^{13}C NMR data show that the naphthalene-to-thiophene bonds of **3a-c** are freely rotating at room temperature. In the ^{1}H NMR of **3a**, two protons at 4- and 4'-positions of the bithiophene ring appear as high as at δ 6.37 ppm probably because of ring current effect induced by two thiophene and naphthalene rings which would be parallel to and perpendicular to the plane of the bithiophene ring, respectively. The six thiophene ring protons also appear at rather higher field of δ 6.5-6.7 ppm (the other two protons at δ 7.10), while **4a**, in which the effects mentioned above are not expected, does not have any absorption at higher field than δ 7.0 ppm. The same holds for **3b, c**. A similar relationship was also observed between **1a-d** and **2a-d**.[2]

X-Ray single crystal structure analysis shows that **3a** adopts the conformation with S_2 symmetry (Fig. 1). Interestingly, the inner bithiophene unit of **3a** is entirely planar, and, in accordance with the conclusion by ^{1}H NMR, the two thiophene rings and one bithiophene ring are approximately parallel to each other with a dihedral angle of about 53° to the planes of the naphthalene rings, and thus they constitute a layered assembly.

The longest λ_{max} for each **3a-c** is slightly greater than that of the corresponding **4a-c** (Table 1), whereas the longest λ_{max} for each **1b-d** is smaller than that of **2b-d** because of twisted conformation between thiophene unit and naphthalene ring.[2,9]

The CV oxidation potentials (Table 1) were determined with a platinum working electrode and 0.1 M electrolyte (tetrabutylammonium perchlorate) in THF (for **4a** and **4b** in CH_3CN). Every compound except **4b** shows irreversible oxidation peaks probably because electro-polymerization takes place.[10] As expected, E^{ox}



Crystal data: $C_{36}H_{22}S_4$, Tetragonal $I4_1/a$
a=13.980(2) Å, c=28.956(3) Å,
V=5659(2) Å^3, Z=8, R=0.085

Fig. 1. ORTEP Drawing of **3a**

Table 1. UV/Vis Spectra and Oxidation Potential Data of **3a-c** and **4a-c**.

Oligothiophenes	λmax (nm) (ε)	E^{ox} (V)^a	Oligothiophenes	λmax (nm) (ε)	E^{ox} (V*)^a
3a	375 (20900) 326 (23700)	0.63	**4a**	357 (30200)	0.76
3b	402 (36400)	0.50	**4b**	393 (40500)	0.62
3c	429 (40000) 346 (46200)	0.44	**4c**	418 (50500)	0.53

a . V *vs.* Ferrocene/Ferrocenium Couple decreases with an increasing number of thiophene rings without any exception. E^{ox} of **3a-c** are lower than those of the corresponding **4a-c**. A similar relationship was observed between **1a-d** and **2a-d** and used as a measure of interactions between two oligothiophene units in **1a-d**.[2] It is thus concluded that radical cation-stabilizing intramolecular interactions among the three (oligo)thiophene units also exist in compounds **3a-c** and contribute to lowering of their E^{ox}.

A partial support for this work by a Grant-in-Aid for the Scientific Research from the Ministry of Education, Science and Culture (No. 05453028), is greatly acknowledged.

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4. **3a**: m.p. 253-255 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 6.37 (d, J 3.6 Hz, 2H), 6.56 (d, J 2.9 Hz, 2H), 6.59 (d, J 3.6 Hz, 2H), 6.69-6.72 (m, 2H), 7.10 (d, J 4.5 Hz, 2H), 7.55 (t, J 7.6 Hz, 4H), 7.61-7.65 (m, 4H), 7.94 (d, J 8.1 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.09, 124.09, 125.12, 125.18, 126.76, 127.91, 128.21, 129.26, 129.38, 130.66, 132.07, 132.12, 132.36, 132.45, 135.48, 136.34, 143.14, 144.06; *m/z* [electron impact (EI)] 582 (M^+).
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7. **3b**: m.p. 232-234 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 6.37 (d, J 3.7 Hz, 2H), 6.56 (dd, J 3.6 and 0.8 Hz, 2H), 6.68 (d, J 3.7 Hz, 2H), 6.69 (dd, J 4.7 and 0.8 Hz, 2H), 6.97 (s, 2H), 7.08 (dd, J 4.7 and 3.6 Hz, 2H), 7.53 (t, J 7.6 Hz, 4H), 7.62 (d, J 7.1 Hz, 4H), 7.93 (d, J 8.1 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.50, 123.71, 124.29, 125.14, 125.24, 126.83, 127.87, 128.39, 129.28, 129.48, 130.57, 131.87, 132.21, 132.34, 132.47, 135.48, 135.71, 136.16, 143.57, 144.07; *m/z* (EI) 664 (M^+).
8. **3c**: m.p. 150-153 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 6.44 (t, J 3.8 Hz, 4H), 6.73 (t, J 4.5 Hz, 4H), 6.93 (d, J 3.6 Hz, 2H), 6.95-6.98 (m, 4H), 7.06 (d, J 3.6 Hz, 2H), 7.16 (d, J 5.0 Hz, 2H), 7.54 (t, J 7.6 Hz,4H), 7.63 (d, J 6.9 Hz, 4H), 7.94 (d, J 8.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.44, 123.72, 123.77, 123.97, 124.04, 124.15, 125.20, 127.67, 128.60, 128.68, 129.57, 129.63, 130.68, 131.73, 131.81, 132.18, 132.20, 135.48, 135.77, 135.94, 136.30, 136.37, 137.56, 143.35, 143.67; *m/z* (FAB) 910 (M^+).
9. A remarkable bathochromic shift, compared with tetramethylthiophene, was observed in the UV spectrum of $[2_4]$(2,3,4,5)thiophenophane (superthiophenophane) (Takeshita, M.; Koike, M.; Tsuzuki, H.; Tashiro, M. *J. Org. Chem.*, **1992**, *57*, 4654). For optical properties (electronic, optical rotatory dispersion, and circular dichromism spectra) of heterohelicenes, see: Groen, M.B.; Wynberg, H. *J. Am. Chem. Soc.*, **1971**, *93*, 2968.
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(*Received in Japan* 1 *November* 1993; *accepted* 24 *January* 1994)