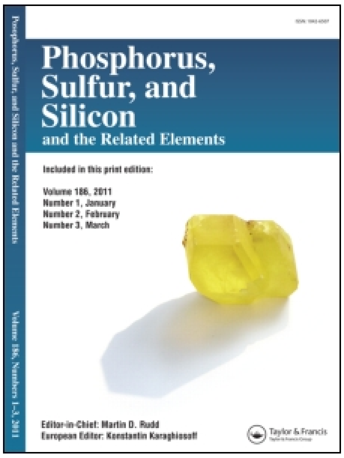

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3,4-Thienylene-ethynylene Oligomers

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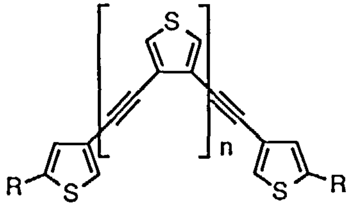
Several well-defined 3,4-thienylene-ethynylene oligomers with different chain lengths have been synthesized and characterized. X-Ray crystallographic analyses proved their unique, totally helical conformations.

KEY WORDS thiophene, acetylene, oligomer, Pd-catalyzed coupling reaction, X-ray analysis, helical conformation

INTRODUCTION

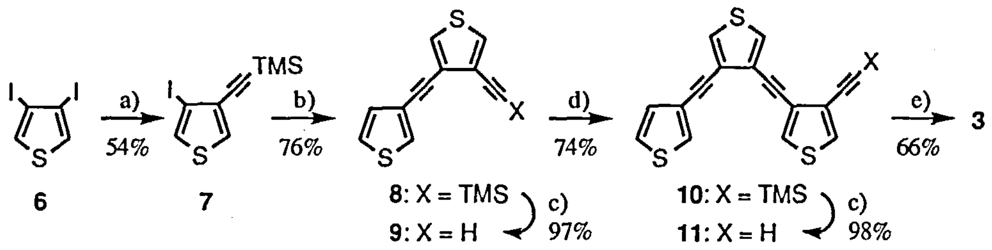
Recently, π-conjugated polymers with the alternate arrangement of arylenes and acetylenes, poly(arylene-ethynylene)s, have received much attention as an important class of materials with potentially interesting optical and electronic properties. The majority of them have been limited to rigid linear *"para"* linkage systems. On the other hand, *"ortho"* linkage pattern on the aromatic ring would lead to more flexible helical systems, which allow not only inter- but also intra-molecular stacking of the π system to occur. Oligo(*o*-phenylene-ethynylene)s have been recently reported as only an example of such compounds.[1] We have designed 3,4-thienylene-ethynylene system (**1–5**), which can hold additional heteroatomic interactions and take unique helical conformations.



1: n = 1, R = H
2: n = 3, R = H
3: n = 5, R = H
4: n = 5, R = $(CH_2)_8CH_3$
5: n = 7, R = $(CH_2)_8CH_3$

RESULTS AND DISCUSSION

The preparation of **3** is outlined in Scheme 1 as a typical synthetic example. The Pd-catalyzed coupling reaction[2] of terminal alkynes and thienyl halides was repeatedly



SCHEME 1 a) TMSC≡CH, $Pd(PPh_3)_4$, CuI, Et_3N, reflux; b) 3-ethynylthiophene, $Pd(PPh_3)_4$, CuI, Et_3N, reflux; c) KF, H_2O/DMF; d) 7, $Pd(PPh_3)_4$, CuI, Et_3N, reflux; e) 3,4-diiodothiophene, $Pd(PPh_3)_4$, CuI, Et_3N, reflux.

applied to the synthesis of these oligomers, which were obtained as stable pale yellow crystals and fully characterized by spectroscopic and elemental analyses.

The solid-state conformations of **2** and **4** were elucidated by an X-ray crystallographic analysis. As shown in Figure 1, they take a totally helical conformation, and the dithienylethynylene moieties stack with each other in parallel with a distance of 3.7 Å. In the crystal of **2**, there exist intermolecular face-to-face overlaps of thiophenes. A detailed comparison of the ^{1}H NMR spectra of the oligomers **2**–**5** with that of **1** revealed high-field shifts of the thienyl protons, supporting that the helical conformation with intramolecular stacking of the thiophene moieties also dominates in solution. Electronic spectra of these oligomers showed a characteristic π-π^* transition with almost identical absorption maximum (λ_{max}/nm in THF, **1**: 262, 294_{sh}; **2**: 262, 293_{sh}; **3**: 262, 302_{sh}; **4**: 265, 303_{sh}; **5**: 263, 303_{sh}). This absorption band showed a only slight hyperchromic shift with the increasing chain length, suggesting hypochromism caused by the interaction between electronic states of chromophores stacked in parallel.

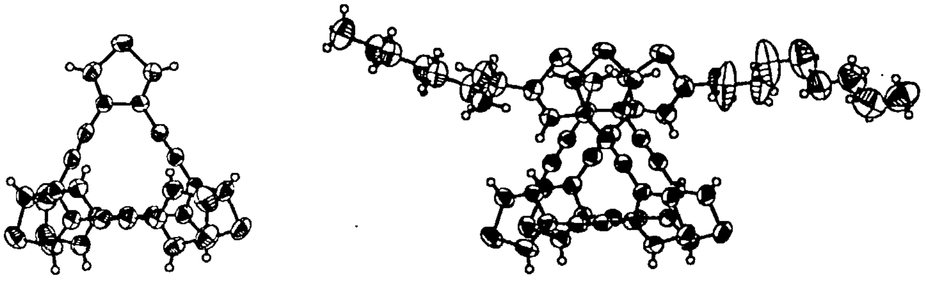


FIGURE 1 ORTEP drawings of **2** (left) and **4** (right).

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