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3,4-Thienylene-ethynylene Oligomers

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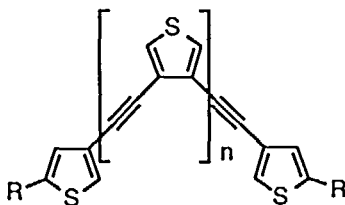
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Several well-defined 3,4-thienylene-ethynylene oligomers with different chain lengths have been synthesized and characterized. X-Ray crystallographic analyses proved their unique, totally helical conformations.

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

INTRODUCTION

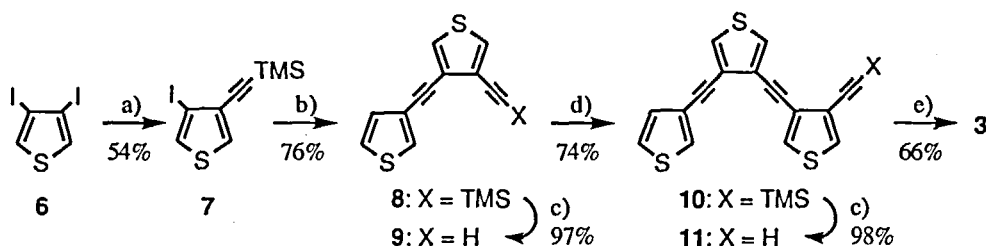
Recently, π -conjugated polymers with the alternate arrangement of arylenes and acetylenes, poly(arylene-ethynylene)s, have received much attention as an important class of materials with potentially interesting optical and electronic properties. The majority of them have been limited to rigid linear "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 reaction² of terminal alkynes and thienyl halides was repeatedly



SCHEME 1 a) $\text{TMSC}\equiv\text{CH}$, $\text{Pd}(\text{PPh}_3)_4$, CuI , Et_3N , reflux; b) 3-ethynylthiophene, $\text{Pd}(\text{PPh}_3)_4$, CuI , Et_3N , reflux; c) KF , $\text{H}_2\text{O}/\text{DMF}$; d) **7**, $\text{Pd}(\text{PPh}_3)_4$, CuI , Et_3N , reflux; e) 3,4-diiodothiophene, $\text{Pd}(\text{PPh}_3)_4$, 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 ^1H 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 ($\lambda_{\text{max}}/\text{nm}$ 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.

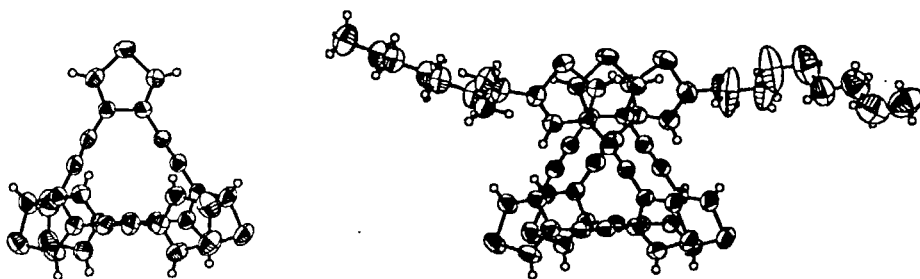


FIGURE 1 ORTEP drawings of **2** (left) and **4** (right).

REFERENCES

1. R. H. Grubbs and D. Kratz, *Chem. Ber.*, **126**, 149 (1993).
2. K. Sonogashira, Y. Tohda, and N. Hagihara, *Tetrahedron Lett.*, **1975**, 4467.