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A new π-system: 1-aryl-2,5-di(2-thienyl)pyrroles

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Abstract

1-Aryl-2,5-di(2-thienyl)pyrroles and their oligomers have been synthesized as a new π-system. UV–vis absorption spectra, X-ray crystallographic analysis, and cyclic voltammogram showed that the present π-system showed good co-planarity and high ability to donate its π-electron.

Keywords: coupling reactions; electron donors; pyrroles; thiophenes.

Development of π-conjugated polymers and oligomers has been a significant subject of many recent studies because of the numerous optical, electrochemical and electrical properties of these compounds.[1] In particular, poly- and oligothiophenes appear to be promising candidates on account of their high chemical and electrochemical stability. Since unsubstituted poly- and oligothiophenes become less soluble in regular organic solvents, alkyl chains are often introduced into the thiophene ring to improve their solubility. However, these chains cause another problem, that is, the co-planarity of the π-conjugated system is diminished.[2] In order to solve this dilemma, our attention was focused on a 1-aryl-2,5-di(2-thienyl)pyrrole system (**I**) as an elementary unit. This new system was expected to have some advantageous points: (i) the central aryl group stands perpendicular to the π-system such that the co-planarity is affected to a lesser extent to cause a bathochromic shift in its UV–vis absorption spectrum.[2c] Indeed, MNDO/PM3 calculation[3] showed that the conformation (**Ia**) is the most favorable for **I** (Ar=phenyl, Y=H); (ii) the perpendicular aryl group impedes the stacking of the π-systems and as a result increases their solubility; (iii) various aryl groups can be employed in order to evolve the physical properties of **I**.

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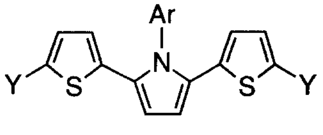

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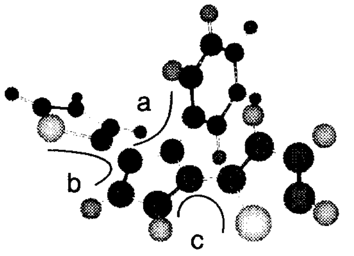
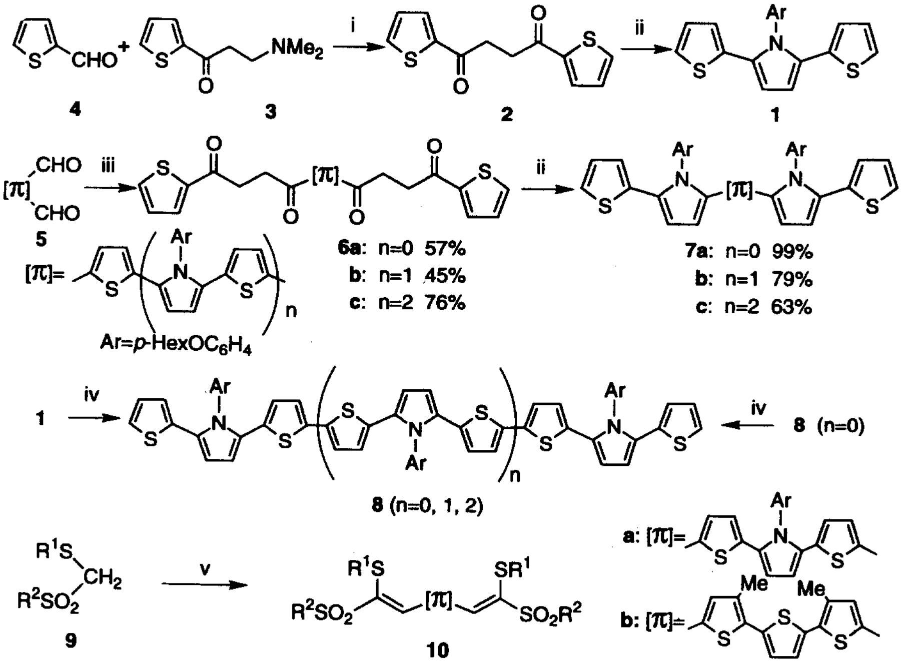


Ia (Ar=Ph, Y=H)

To our surprise, 1-alkyl-2,5-di(2-thienyl)pyrroles and their oligomers have been reported,[4] but we could not find 1-aryl-2,5-di(2-thienyl)pyrroles in the literature. Here we report a synthetic route leading to 1-aryl-2,5-di(2-thienyl)pyrroles and their oligomers as well as their physical properties, including third-order optical non-linearity.

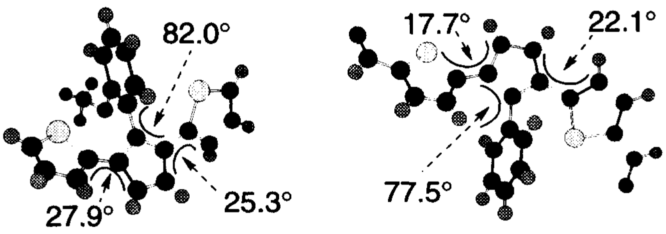
Scheme 1 summarizes the fundamental synthetic sequence employed herein: 1-aryl-2,5-di(2-thienyl)pyrroles (**1**) were prepared by Paal–Knorr condensation[5] of various aniline derivatives with 1,4-di(2-thienyl)-1,4-butanedione (**2**),[5c] which was easily obtainable from 2-thiophenecarbaldehyde and a Mannich base (**3**) (Stetter reaction),[6] in the presence of acetic acid under azeotropic conditions. Application of this sequence to dicarbaldehydes (**5a**, **5b**, and **5c**) gave three kinds of new π-systems (**7a**, **7b**, and **7c**, respectively). The starting **5b** and **5c** were synthesized by diformylation of **1** and **7a**, respectively. Another route was the oxidative coupling of **1**: lithiation of **1** with *n*-BuLi followed by treatment with $CuCl_2$ (−78°C/30 min) gave a dimeric product [**8** (n=0); 48% yield] along with a trimer [**8** (n=1); 6% yield] and **1** (25% yield). On a similar $CuCl_2$ treatment (−78°C/30 min, then rt/30 min) of a dimeric derivative of **8** (n=0), we could isolate the corresponding tetramer **8** (n=2) in 22% yield. Since the compounds synthesized herein were easily soluble in such organic solvents as ethanol, chloroform, THF, and benzene, we could functionalize their new π-systems without any problem. For example, their



Scheme 1. (i) NaCN/DMF, (ii) $ArNH_2$/toluene–AcOH (reflux), (iii) **3**+NaCN/DMF, (iv) *n*-BuLi/THF then $CuCl_2$, (v) *n*-BuLi, TMSCl/THF, −78°C then **5a** or **5b**

derivation into the ketene dithioacetal *S,S*-dioxide derivatives (**10**) was easily achieved according to Scheme 1.[7]

The above expectation that the 1-aryl group stands perpendicular to the 2,5-di(2-thienyl)-pyrrole π-system was supported by a UV–vis absorption spectrum of **1** (Ar=*p*-methoxyphenyl), which showed λ_{max} at a longer wavelength [338 nm (ε 21400) in THF] in comparison with those of 1-methyl-2,5-di(2-thienyl)pyrrole [324 nm (ε 18100)] and 1-isopropyl-2,5-di(2-thienyl)pyrrole [303 nm (ε 12200)]. Single-crystal X-ray crystallographic analyses[8,9] of **1** (Ar=*m*-methoxyphenyl) and **5a** (Ar=phenyl) (Fig. 1) showed that the thiophene rings at both sides were slightly distorted from the central pyrrole plane; thus, the co-planarity of the π-system was lost to some extent.



1 (Ar=*o*-MeOC$_6$H$_4$) **5a** (Ar=Ph)

Figure 1. Molecular structures by X-ray analyses and their torsion angles between π-planes

The UV–vis absorption spectra of **1**, **7**, and **8** in THF are summarized in Table 1. It is apparently shown that the absorption maximum (λ_{max}) is shifted toward longer wavelength with the increase of heteroaromatic rings to approach the maximum value. This tendency is very similar to that reported in the oligothiophenes.[10]

Cyclic voltammograms of these compounds were also measured at a platinum electrode in a 0.1 M acetonitrile solution of tetrabutylammonium perchlorate (TBAP). As shown in Table 2, we observed one irreversible couple for **1** (Ar=*p*-methoxyphenyl) and one reversible couple for **5b** (Ar=*p*-methoxyphenyl), **10a** (Ar=*p*-methoxyphenyl, R^1=Me, R^2=*p*-Tol), and **10b** (R^1=Me, R^2=*p*-Tol). These imply that the replacement of the thiophene ring by a pyrrole ring makes the oxidation potential lower. In the ^{1}H NMR (300 MHz) of **10a** (Ar=*p*-methoxyphenyl, R^1=Me, R^2=*p*-Tol) in $CDCl_3$, a small amount of iodine broadened signals for the heteroaromatic protons except for the 4-positions of the thiophene rings. As the amount of the added iodine increased, the signals became more broad and finally disappeared. The broad peaks came back to the original sharp peaks with an excess amount of sodium thiosulfate ($Na_2S_2O_3$). In contrast, the addition of iodine (more than 2 mol equiv.) did not broaden the proton signals of **5b** (Ar=*p*-methoxyphenyl) and **10b** (R^1=Me, R^2=*p*-Tol). It should be noted that compounds **7** (Ar=*p*-

Table 1
UV–vis absorption spectral data in THF

Total number of heterocycles	Compound[a]	λmax/nm (ε)	λmax/nm of the corresponding oligothiophene
3	**1**	340 (21700)	345,[b] 354[c]
5	**7a**	394 (38500)	412,[b] 416[c]
6	**8** (n=0)	422 (45700)	434[c]
7	**7b**	412 (55800)	440[b]
9	**7c**	435 (66800)	455[b]
9	**8** (n=1)	449 (58700)	455[b]
12	**8** (n=2)	455 (74000)	456[d]

[a] Ar=*p*-hexyloxyphenyl, [b] ref. 10a, [c] ref. 10b, [d] ref. 10c.

Table 2
The first oxidation potential[a]

Compound[b]	E_{pa}/V
1	0.41[c]
5b	0.76
10a	0.54
10b	0.84

[a] for compounds vs. Ag/Ag^+ in 0.1 M TBAP in CH_3CN. Scan rate: 100 mV s^{-1}. [b] Ar=*p*-$MeOC_6H_4$. [c] An irreversible couple.

hexyloxyphenyl) and **8** (Ar=*p*-hexyloxyphenyl) show broad signals for all of the protons except for those of the *p*-hexyloxyphenyl rings in undegassed $CDCl_3$, even if iodine is absent.

We have already reported an acceptor–donor–acceptor type of non-linear optics (**10b**) which have an electron-donating terthiophene-based π-system at the center and electron-accepting ketene dithioacetal *S,S*-dioxide moieties at both ends.[11] Although the compound (**10b**; R^1=Me, R^2=*p*-Tol) showed the maximum $\chi^{(3)}$ value (relative to that of CS_2: 1000) which was evaluated by measurement of the solutions optical Kerr effect near the absorption edge, their slight solubility in regular organic solvents prevented further research and development. Therefore, we decided to employ the 1-aryl-2,5-di(2-thienyl)pyrrole system as the central donor site. Here we wish to describe a preliminary result. Among various derivatives of **10a** (Ar=*o*-, *m*-, or *p*-methoxyphenyl, phenyl, *p*-chlorophenyl; R^1=R^2=Me, *p*-tolyl, *p*-methoxyphenyl, or *p*-chlorophenyl), **10a** (Ar=*m*-methoxyphenyl, R^1=R^2=*p*-tolyl) gave the best $\chi^{(3)}$ value (relative to that of CS_2: 2700 in THF; 3300 in DMSO). These values correspond to 2.7 and 3.3×10^{-9} esu, respectively, which are the largest for the third-order non-linear optics with relatively lower molecular weight.

We are continuing our investigation to utilize the present new π-system for developing various functionalized materials.

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