

Synthesis and UV-visible properties of thienyl- substituted pyrrole azo dyes

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Abstract- The synthesis of thienyl- substituted pyrrole azo dyes and their UV-visible properties are described.

Keywords: pyrroles, thienylpyrroles, azo dyes, UV-visible study, nonlinear optics (NLO).

Introduction

The design and synthesis of organic chromophores as nonlinear optical (NLO) materials has attracted much attention in recent years.¹⁻² They have great potential especially for use in optical communication, information processing, frequency doubling and integrated optics.³ Organic NLO materials have many advantages over inorganic materials, such as large nonlinear optical coefficients, greater ease for synthetic design, easy preparation and lower cost.⁴⁻⁵ It has been revealed that the second order hiperpolarizabilities (β) of heterocyclic chromophores are often higher than their benzene analogues.⁶⁻⁷ Recently we have also demonstrated that donor-acceptor substituted bithiophenes and terthiophenes have many favorable features as NLO materials.⁸⁻¹⁰ Employment of conjugated thiophene and pyrrole derivatives as donors combined with substituted acceptor groups are promising candidates among such D-A systems due to their numerous applications. Unlike the thiophene or furan analogues, the pyrrole ring can be further substituted on the nitrogen atom so that the electron density of the chromophore can be changed, which should have significant influence on the NLO properties.¹¹⁻¹⁵

As part of our continuing interest in non-linear optical material^{8-10,16} we report in this paper the synthesis and the UV-visible study of new 1-alkyl(aryl)-2-(thieno-2-yl)-5-phenylazopyrrole derivatives **3-6** which have the 4-CO₂Me, 4-CN, 4-NO₂ and 2,4-[NO₂]₂ groups as the electron-withdrawing groups on the phenylazo moiety and the conjugated 1-alkyl(aryl)-2-(thieno-2-yl)pyrrole, as strong π -electron donor moieties.

Results and discussion

Synthesis

Recently we have reported the synthesis of 1-alkyl(aryl)-2-(thieno-2-yl)pyrroles **1** through a combination of the Friedel-Crafts and the Lawesson reactions.¹⁷ These compounds **1** have proved to be versatile substrates in azo coupling reactions, allowing the preparation of several new donor-acceptor substituted thienylpyrroles.

The synthesis of thienylpyrrole azo dyes **3-6** is outlined in Scheme 1. The coupling reaction of aryldiazonium salts **2a-d** (Figure 1), with 1-alkyl(aryl)-2-(thieno-2-yl)pyrroles **1a-b** give rise to the formation of 1-alkyl(aryl)-2-(thieno-2-yl)-5-phenylazopyrrole derivatives **3-6**. This functionalization was made by reacting the activated thienyl pyrroles **1a-b** with aryldiazonium salts in acetonitrile/acetic acid for 2h at 0 °C.

The relative reactivity of thiophene and pyrrole electron-rich heterocycles is well established as pyrrole > furan > thiophene, and this has been confirmed by the diazotisation of thienylpyrroles **1**. Due to the greater reactivity of pyrrole ring with electrophiles¹⁸ the introduction of phenylazo group as the acceptor unit to the skeleton of **1** occurred exclusively on the pyrrole ring to give 1-alkyl(aryl)-2-(thieno-2-yl)-5-phenylazopyrrole **3-6** in good yields (47-85%), (Scheme 1, Table 1).

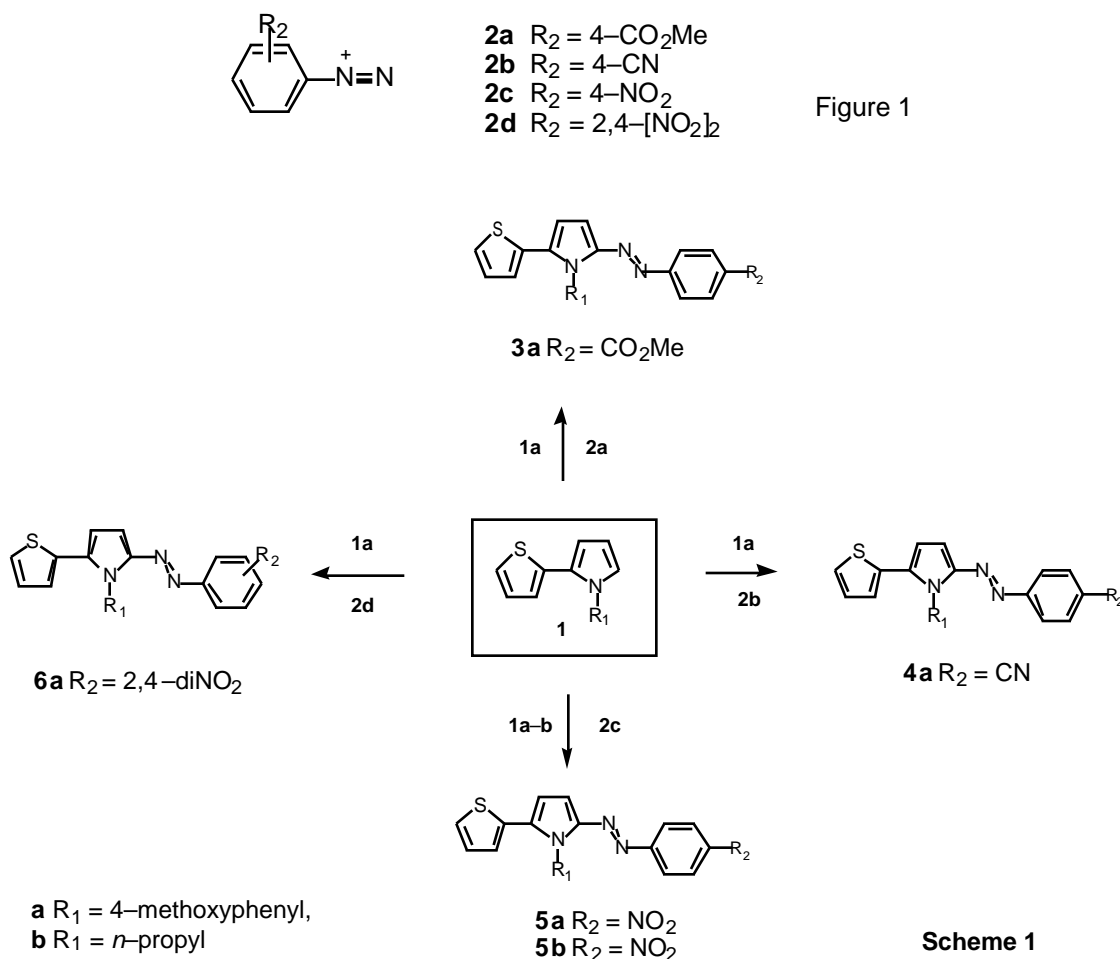


Table 1. Yields and UV-vis. absorption spectra of pyrrole azo dyes **3-6**.

Entry	Compound	R ₁	R ₂	Yield (%)	UV/Vis. (Ethanol) λ_{max} [nm] (ϵ)	$h\nu_{\text{ICT}}$ [eV]
1	3a	4-Methoxyphenyl	4-CO ₂ Me	85	469.5 (30923)	2.64
2	4a	4-Methoxyphenyl	4-CN	84	475.5 (28628)	2.61
3	5a	4-Methoxyphenyl	4-NO ₂	81	500.0 (27165)	2.48
4	5b	<i>n</i> -Propyl	4-NO ₂	63	486.0 (27750)	2.55
5	6a	4-Methoxyphenyl	2,4-diNO ₂	47	528.0 (32614)	2.35

UV-visible study

Electronic absorption spectra of all push-pull compounds **3-6** show an intense lowest energy charge-transfer absorption band in the UV-visible region. The position of this band is strongly influenced by the structure of the compounds, for example by the type of substitution pattern in the donor and the acceptor moieties. Communication between the electron donating and accepting termini can be evaluated by comparing the λ_{max} values.

The influence of the strength of the acceptor group is demonstrated by comparison of the absorption maxima of compounds **3a** and **6a** as the longest wavelength transition is shifted from 469.5 nm in 1-(4-methoxyphenyl)-2-(thieno-2-yl)-5-(4-carbomethoxyphenylazo)pyrrole **3a** (Table 1, entry 1) to 528.0 nm for 1-(4-methoxyphenyl)-2-(thieno-2-yl)-5-(2,4-dinitrophenylazo)pyrrole **6a** (Table 1, entry 5). Figure 2 demonstrates the influence of the acceptor group on absorption maxima for the 1-aryl-2-(thieno-2-yl)-5-phenylazopyrrole series. This effect has been attributed to the stabilization of LUMO by the electron-withdrawing groups.¹⁹ The influence of the substituent on the nitrogen atom of the pyrrole ring is demonstrated by comparison of the absorption maxima of compounds **5a** and **5b** as the longest wavelength transition is shifted from 486.0 nm in 1-(*n*-propyl)-2-(thieno-2-yl)-5-(4-nitrophenylazo)pyrrole **5b** (Table 1, entry 4) to 500.0 nm for 1-(4-methoxyphenyl)-2-(thieno-2-yl)-5-(4-nitrophenylazo)pyrrole **5a** (Table 1, entry 3). Figure 3 demonstrate the influence of the substituent on the nitrogen atom of the pyrrole ring on absorption maxima for the 1-alkyl(aryl)-2-(thieno-2-yl)-5-phenylazopyrrole series. In general, the stronger the donor and/or acceptor group, the smaller the energy difference between ground and excited states, and the longer the wavelength of absorption.²⁰ According to Zyss¹ the increase of the β values characteristic of the NLO effects is

accompanied by an increase of the λ_{max} in the UV-visible spectra, i.e. a decrease in the intramolecular charge transfer (ICT) values.

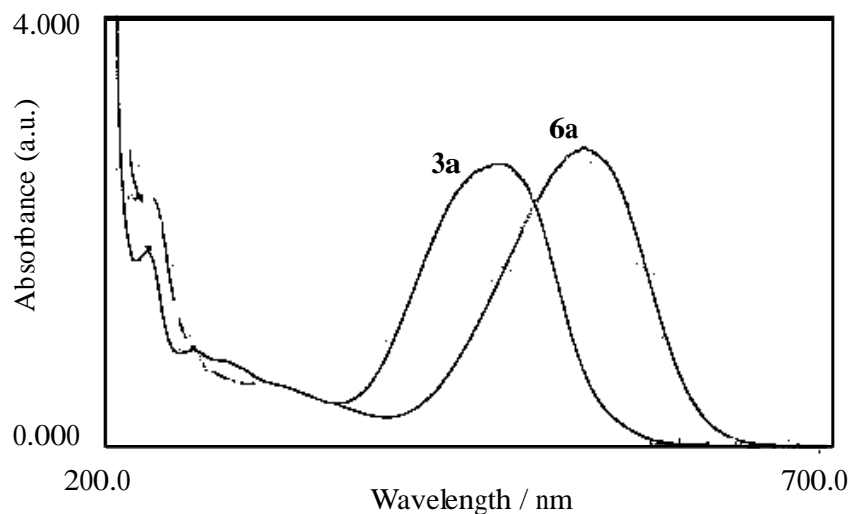


Figure 2 – UV-visible spectra of compounds **3a** and **6a** recorded in ethanol, demonstrating the electron-withdrawing effect of the acceptor group on the absorption maxima.

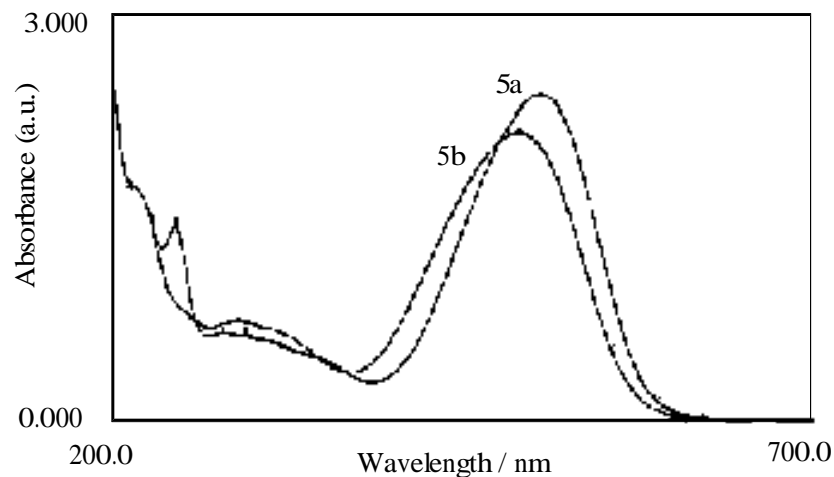


Figure 3 – UV-visible spectra of compounds **5a** and **5b** recorded in ethanol, demonstrating the effect of the substituent on the nitrogen atom of the pyrrole ring on the absorption maxima.

Compounds **3-6** were completely characterized by elemental analysis and/or HRMS, ^1H NMR and ^{13}C NMR spectroscopy and UV-visible and IR spectroscopy.

The examination of the solvatochromic, the electrochemical and the non-linear optical properties of the new push-pull systems **3-6** will be investigated in the future.

Conclusions

In summary, we have achieved the first synthesis of a series of thienyl-substituted pyrrole azo dyes **3-6**, and have measured their UV-visible absorptions. By comparing the derivatives synthesized, it can be seen that the withdrawing group on the phenylazo moiety and the type of substituent on the nitrogen atom of the pyrrole ring has significant influence on the UV-visible properties.

In agreement with previous findings^{11,13,15} the new compounds prepared can be applied for the manufacture of new materials with strong non-linear optical (NLO) properties.

Experimental

Coupling of the thienyl pyrroles 1a-b with 4-carbomethoxy-, 4-cyano- and 4-nitro-substituted benzenediazonium salts 2a-c (general procedure).

i) Diazotisation of 4-carbomethoxy-, 4-cyano- and 4-nitroaniline

Aniline (4.0 mmol) was pasted with NaNO₂ (4.0 mmol) and water (10 ml) to a smooth slurry and it was added to a well-stirred mixture of HCl (d = 1.18; 3 ml) and ice (3 g) at 0 - 5 °C. The reaction mixture was stirred for 30min.

ii) Coupling reaction with thienyl pyrroles 1a-b

The diazonium salt solution previously prepared (4.0 mmol) was added drop wise to the solution of thienyl pyrroles **1** (4.0 mmol) in acetonitrile (50 ml) and some drops of acetic acid. The combined solution was maintained at 0 °C for 2 h with stirring. After this time the resulting mixture was diluted with petrol ether (20 ml) and water (40 ml) and the product formed was isolated by filtration. The organic layer was diluted with chloroform, washed with water and dried with anhydrous MgSO₄. The dried solution was evaporated and the remaining 1-alkyl(aryl)-2-(2'-thienyl)-5-phenylazopyrroles **3-6** were purified by column chromatography on silica with increasing amounts of ether in light petroleum (b.p. 40-60 °C) as eluent.

Synthesis of 1-(4-methoxyphenyl)-2-(thieno-2-yl)-5-(4-nitrophenylazo)pyrrole **5a** (example).

Compound **5a** was obtained in a 81% yield as a violet solid with gold luster, mp 176-179 °C; ¹H NMR (acetone-d₆) δ 3.95 (s, 3H, OCH₃), 6.97 (d, 1H, *J*=4.5 Hz, 3-H), 7.02-7.06 (m, 1H, 4'-H), 7.08 (d, 1H, *J*=4.5 Hz, 4-H) 7.13 (dd, 1H, *J*=3.9 and 1.2 Hz, 3'-H), 7.16 (d, 2H, 9.0 Hz, 2xAr-H), 7.45 (d, 2H, 9.0 Hz, 2xAr-H), 7.48 (dd, 1H, *J*=5.1 and 1.2 Hz, 5'-H), 7.71 (d, 2H, 9.2 Hz, 2xAr-H), 8.29 (d, 2H, 9.2 Hz, 2xAr-H); ¹³C NMR (DMSO-d₆) δ 55.6, 103.5, 113.1, 114.5, 121.9, 125.2, 125.7, 128.3, 128.7, 130.7, 132.2, 137.3, 146.5, 149.7, 156.8, 160.0; IR (Nujol) ν 3051, 2568, 1569, 1546, 1509, 1490, 1436, 1429, 1421, 1366, 1338, 1291, 1253, 1243, 1233, 1196, 1166, 1109, 1149, 1091, 1018, 982, 963, 850, 815, 771, 748, 734 cm⁻¹; UV (EtOH): λ_{max} nm (εM⁻¹cm⁻¹) 500.0

(27165), 227.5 (15871). *Anal.* Calcd for C₂₁H₁₆N₄O₃S: C, 62.38; H, 4.06; N, 13.60; S, 7.92. Found: C, 62.37; H, 3.96; N, 13.86; S, 7.93.

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