

Synthesis and Second-Order Nonlinearities of Sulfonyl-Substituted Pyrrole Imino Dyes

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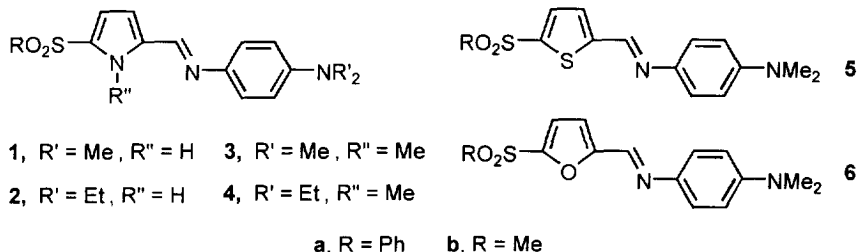
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ABSTRACT: The first synthesis of sulfonyl-substituted pyrrole imino dyes **1-4** and their UV-VIS absorptions, second-order nonlinear optical properties and thermal stabilities are described, and compared with those of the thiophene and furan analogues **5-6**.

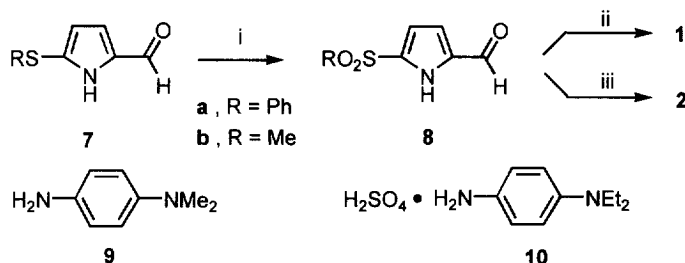
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The design and synthesis of organic chromophores as nonlinear optical (NLO) materials has attracted much attention in recent years.^{1,2} They have great potential especially for use in optical communication, information processing, frequency doubling and integrated optics.³ Organic NLO materials have many advantages as compared to inorganic materials, such as higher second-order nonlinearities, lower response time and greater ease for synthetic design.^{4,5} It has been shown that molecular hyperpolarizabilities ($\mu\beta$) of thiophene-containing chromophores are often higher than their benzene analogues.⁶ We have recently demonstrated that sulfonyl-substituted thiophene⁷ and furan compounds⁸ have many favorable features as NLO materials. So far, however, there is only one report on the use of pyrrole-containing chromophores as second-order NLO materials.⁹

In this paper we describe the first synthesis, UV-VIS absorptions, second-order NLO properties and thermal stabilities of pyrrole imino dyes **1-4** which have the sulfonyl group as the electron-withdrawing group on the pyrrole ring to impart better transparency in the visible spectrum and the amino group as the electron-donating group to increase the polarisation of the chromophore.¹⁰ 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. In addition, replacing N-H group of the pyrrole ring with another substituent would eliminate some intermolecular hydrogen bondings which might also affect their macroscopic structures and NLO properties. We will compare various properties of pyrroles **1-4** with those of thiophenes **5** and furans **6**, and will be able for the first time to compare the experimental results with theoretical calculations.

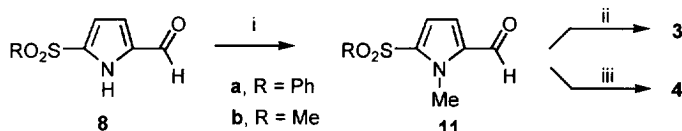


The synthesis of these sulfonyl-substituted pyrrole imino dyes **1-4** is shown in Scheme 1. The sulfide compounds **7** as prepared in four steps from pyrrole-2-carbaldehyde¹¹ were oxidized by MCPBA to the corresponding sulfones **8**. Condensation of compounds **8** with amines **9** and **10** then gave the desired products **1** and **2**, respectively in good yields.



Scheme 1 Reagents and conditions : i, MCPBA (3eq), CH₂Cl₂, 0 °C; ii, **9**, H₂SO₄, 25 °C; iii, **10**, Et₃N, CH₂Cl₂, 25 °C.

Attempted acylation or sulfonylation of the nitrogen atom of pyrroles **8** with acyl halides, anhydrides or sulfonyl chlorides under various conditions only resulted in the reaction at the oxygen atom.¹² It was found, however, that treatment of **8** with ethyldiisopropylamine¹³ and a catalytic amount of *N,N*-dimethylaminopyridine (DMAP) followed by reaction with methyl iodide gave the *N*-methylated products **11** in good yields (Scheme 2). Condensation of compounds **11** with amines **9** and **10** gave the desired *N*-methylated pyrrole imino dyes **3** and **4**.



Scheme 2 Reagents and conditions: i. (a) (i-Pr)₂NEt (1.2 eq), DMAP (0.2 eq), CH₂Cl₂, 25 °C; (b) MeI (3 eq), 25 °C; ii, **9**, H₂SO₄, 25 °C; iii, **10**, Et₃N, CH₂Cl₂, 25 °C.

The UV-VIS absorptions of compounds **1-4** show that the λ_{\max} values obtained in dioxane are all below 402 nm, and have virtually no absorption above 480 nm as judged by their λ_{cutoff} values (Table 1). The phenylsulfones **1a-4a** have slightly higher λ_{\max} values (6-7 nm) and thus lower charge-transfer energies than the corresponding methylsulfones **1b-4b**. It is interesting to note that polar solvents have opposite effects on the λ_{\max} values of pyrroles **1-2** and their *N*-methylated derivatives **3-4**: blue shift for the former and red shift for the latter.¹⁴ Previously we only observed red shift by polar solvents for the thiophene⁷ and furan⁸ imino dyes **6**. It should also be pointed out that the λ_{\max} values show the order: thiophene > furan > pyrrole (compare **1a**, **5a**, **6a**; **1b**, **5b**, **6b**). The *N*-methylated pyrroles **3-4** have higher λ_{\max} values than the corresponding parent pyrroles **1-2**. All these novel UV-VIS absorption phenomena highlight the unusual structure and properties of pyrroles as compared to their thiophene and furan analogues.

The molecular hyperpolarizabilities ($\mu_{\beta}\beta$) of chromophores **1-4** were estimated by solvatochromism.¹⁵ The zero-frequency $\mu_{\beta}\beta_0$ values were corrected with a two-level model.¹⁶ It is quite remarkable that pyrroles

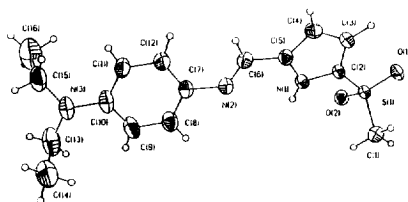
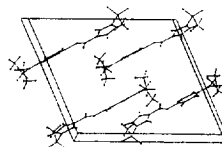
Table 1 UV-Vis absorptions, μ_{eg} , μ_g ($\mu_e - \mu_g$), $\mu_g\beta$, $\mu_g\beta_0$ values for PNA and compounds **1-6**.

Compound	$\lambda_{max}^a/$ nm	$\lambda_{cutoff}^a/$ nm	$\mu_{eg}/$ Debye	μ_g ($\mu_e - \mu_g$)/ Debye ²	$\mu_g\beta^b/$ 10 ⁻⁴⁸ esu	$\mu_g\beta_0/$ 10 ⁻⁴⁸ esu	SHG intensity ^{c/} [$I(2\omega)_{sample} / I(2\omega)_{quartz}$]	$T_d^d/$ °C
1a	392	461	6.8	-48	-114	-45	0	173
1b	386	469	5.4	-67	-90	-37	0	188
2a	400	460	5.6	-84	-152	-57	2.9	178
2b	393	480	6.0	-105	-194	-76	0	184
3a	394	470	6.5	55	119	46	0.6	300
3b	387	470	6.3	51	94	38	0.35	252
4a	402	478	6.1	103	224	83	0	304
4b	396	470	5.8	76	136	52	0	200
5a ^e	429	509	8.0	148	769 (458) ^g	225 (135) ^g	—	286
5b ^e	422	495	7.2	97	384 (361) ^g	120 (113) ^g	—	295
6a ^f	409	480	6.0	71	502	168	—	223
6b ^f	406	497	6.0	51	320	115	—	220
PNA	352	—	4.7	54	110	55	0	—

^aMeasured in dioxane. ^bEstimated for a fundamental wavelength of 1064 nm. ^cMeasured with quartz as the reference at 800 V. ^dHeating rate of 10 °C/min, heating range of 50 - 800 °C. ^eref. 7. ^fref. 8. ^gMeasured by EFISH with a fundamental wavelength of 1064 nm.

1-2 have negative values of $\mu_g\beta_0$ whereas the *N*-methylated pyrroles **3-4** have positive values. The NEt_2 donating group was found to give higher values of $\mu_g\beta_0$ than the NMe_2 group. The phenylsulfonyl group on the pyrrole ring in most cases leads to higher values of $\mu_g\beta_0$ than the methylsulfonyl group. It is interesting to note that both the λ_{max} values and $\mu_g\beta_0$ values follow the order: thiophene > furan > pyrrole. This is in agreement with the theoretical calculations.¹⁷

The Kurtz powder method was used to determine the averaged second harmonic generation (SHG) intensity using quartz as the reference.¹⁸ Of the eight compounds measured for **1-4**, only **2a**, **3a** and **3b** showed significant SHG intensities; among them only **2a** had higher SHG value than that of quartz. We have so far obtained only the single crystal X-ray structure for **2b** (Fig.1)¹⁹ which shows the *E* configuration about the C=N bond and a dihedral angle of 16.57° between the benzene and the pyrrole ring. The imino nitrogen is *cis* to the pyrrole nitrogen. Compound **2b** has a centrosymmetric alignment with $P2_1/c$ space group (Fig.2) in agreement with the observed zero SHG value.

**Fig.1** X-ray crystal structure of **2b****Fig.2** Packing drawing of compound **2b**

The decomposition temperatures (T_d) of **1-4** were measured by thermogravimetric analysis (TGA) at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. It can be seen that the phenylsulfonyl-substituted pyrrole imino dyes have higher T_d than the methylsulfonyl derivatives. It is also interesting to note that the T_d follows the order: thiophene > furan > pyrrole. However, *N*-methylation of the pyrrole ring increases the T_d significantly ($83\text{ }^\circ\text{C}$ in average). This indicates that the *N*-Me group is thermally more stable than the *N*-H group.

In summary, we have achieved the first synthesis of a series of sulfonyl-substituted pyrrole imino dyes **1-4**, and have measured their UV-VIS absorptions, second-order nonlinearities and decomposition temperatures. By comparing the thiophene, furan and pyrrole analogues, it can be seen that the heteroatom has significant influence on the UV-VIS absorptions, NLO properties and thermal stabilities.

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- $\lambda_{\text{max}}/\text{nm}$ for **1a**: 383 (DMSO), 374 (DMF), 393 (MeOH), 401 (CH_2Cl_2), 391 (THF), 392 (Dioxane). For **3a**: 402 (DMSO), 398 (DMF), 395 (MeOH), 399 (CH_2Cl_2), 395 (THF), 394 (Dioxane).
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- Crystal data for $\text{C}_{16}\text{H}_{21}\text{N}_3\text{O}_2\text{S}$ (**2b**): fw 319.40, Monoclinic, space group $\text{P}2_1/\text{c}$, $a = 14.397(3)\text{ \AA}$, $b = 7.728(1)\text{ \AA}$, $c = 16.809(4)\text{ \AA}$, $\beta = 114.06(2)^\circ$, $V = 1707.7(8)\text{ \AA}^3$, $Z = 4$, $\mu = 7.1073\text{ cm}^{-1}$, Mo K_α radiation ($\lambda = 0.71073\text{ \AA}$), $d_{\text{calcd}} = 1.242\text{ g/cm}^3$, 298 K, $F(000) = 680.$, Siemens P4 diffractometer, orange crystal ($0.4 \times 0.4 \times 0.5\text{ mm}$). Hydrogen atoms were refined freely with isotropical displacement parameters, $R_f = 0.0544$, $R_w = 0.0631$.