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Synthesis of novel sulfonyl-substituted pyrrole chromophores for second-order nonlinear optics

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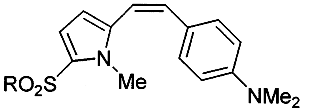
Abstract—The first synthesis of sulfonyl-substituted pyrrole chromophores **1**–**4** and their UV–vis absorptions, second-order nonlinear optical properties and thermal stability are described and compared with those of the benzene, thiophene and furan analogues **5**–**9**. © 2001 Elsevier Science Ltd. All rights reserved.

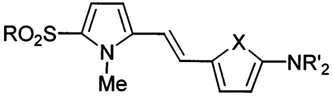
The design and synthesis of organic chromophores as nonlinear optical (NLO) materials have attracted much attention in recent years.[1,2] They have great potential especially for use in optical communication, information processing, frequency doubling and integrated optics.[3] Organic NLO materials have 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 product of dipole moment and molecular hyperpolarizabilities ($\mu\beta$) of heterocyclic chromophores are often higher than their benzene analogues.[6] We have also demonstrated that sulfonyl-substituted thiophene[7] and furan chromophores[8] have many favorable features as NLO materials. Most recently, we have reported the first synthesis of some pyrrole-containing chromophores with a π-bridge of C=N.[9] However, these C=N compounds are rather prone to hydrolytic decomposition. Thus, we want to improve the stability of these compounds by replacing with a C=C π-bridge.

In this paper we describe the first synthesis, UV–vis absorptions, second-order NLO properties and thermal stability of pyrrole chromophores **1**–**4** bearing the π-bridge of C=C which have the sulfonyl group as the electron-withdrawing group on the pyrrole ring and the amino group as the electron-donating group to increase the polarization of the chromophore. Although the sulfone group is not a particularly strong acceptor substituent, it is synthetically more flexible and has broader transparency range in the visible spectrum.[10] From our previous experiences,[9] we have substituted a methyl group on the pyrrole nitrogen in order to increase the thermal stability of these compounds. We will also compare various properties of pyrroles **1**–**4** with those of benzene, thiophene and furan compounds **5**–**9**.[7–9]

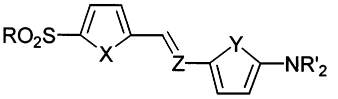
The synthesis of these sulfonyl-substituted pyrrole chromophores **1**–**4** is shown in Scheme 1. Reduction of aldehydes **12** and **15**[9] with sodium borohydride gave the alcohols **13** and **16**, respectively. Treatment of these alcohols with triphenylphosphine hydrobromide gave the phosphonium salts **14** and **17**.[11] Deprotonation of **14** with *n*-BuLi followed by reaction with aldehydes **15** gave only the *cis* products **1a** and **1b**, which are



1



2, R' = Me , X = CH=CH
3, R' = Et , X = S
4, R' = Et , X = O



5, R' = Me , X = S , Y = CH=CH , Z = CH
6, R' = Me , X = O , Y = CH=CH , Z = CH
7, R' = Et , X = S , Y = S , Z = CH
8, R' = Et , X = O , Y = S , Z = CH
9, R' = Me , X = NMe , Y = CH=CH , Z = N

a, R = Ph **b**, R = Me

Keywords: pyrroles; heterocyclic compounds; sulfones; nonlinear optics.

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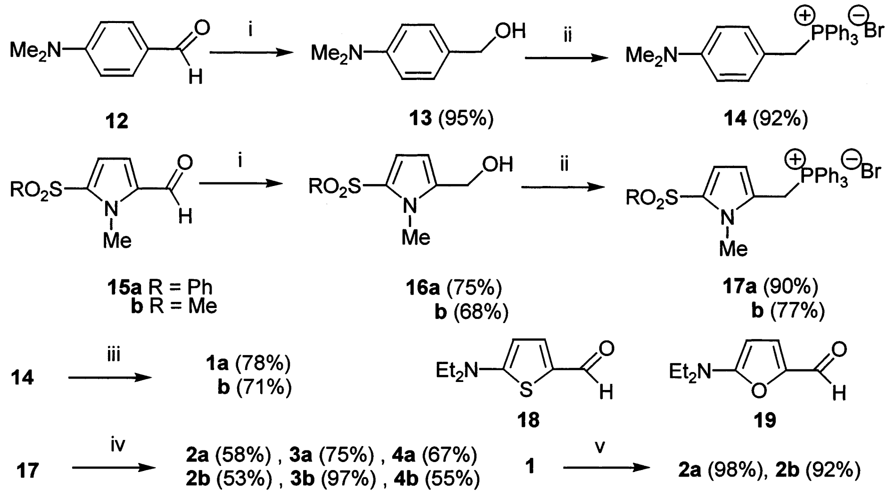
expected from nonstabilized ylides.[12] On the other hand, the Wittig reaction of the stabilized ylide derived from phosphonium salts **17** with aldehydes **12**, **18** and **19** gave predominantly the *trans* products **2**, **3** and **4**, respectively.[13] The *cis* compounds **1** can also be converted to the more stable *trans* products **2** by treatment with a catalytic amount of iodine in refluxing toluene.

The UV–vis absorptions of compounds **1**–**4** show that the λ_{max} values (in dioxane) are all below 370 nm, and have virtually no absorption above 480 nm, as judged by their λ_{cutoff} values (Table 1). The phenyl sulfones **1a**–**4a** have slightly longer λ_{max} values (2–10 nm) and thus lower charge-transfer energies than the methyl sulfones **1b**–**4b**. Polar solvents cause a red shift of the λ_{max} values of compounds **1**–**4** more significantly for the phenyl sulfones than the methyl sulfones. It is important to note that the λ_{max} values of the heterocyclic chromophores follow the order thiophene>furan>pyrrole; for example, **5a**, 403 nm; **6a**, 385 nm; **2a**, 366 nm; **7a**, 450 nm; **8a**, 435 nm; **3a**, 370 nm. The λ_{max} values of the pyrrole compounds show that *trans*->*cis*-C=C (e.g. **2a**, 366 nm; **1a**, 347 nm; **2b**, 364 nm; **1b**, 337 nm) and C=N>C=C (e.g. **9a**, 394 nm; **2a**, 366 nm; **9b**, 387 nm; **2b**, 364 nm).



Scheme 1. *Reagents and conditions*: (i) $NaBH_4$ (0.6 equiv.), methanol, 60°C, 2.5 h (for **13**), or 0°C, 0.5 h (for **16a**), or 0°C, 2.5 h (for **16b**); (ii) $PPh_3 \cdot HBr$ (1 equiv.), CH_2Cl_2, reflux, 4 h (for **14** and **17a**), or CH_2Cl_2/CH_3CN, reflux, 4 h (for **17b**); (iii) (a) 1.6 M *n*-BuLi (1.2 equiv.), Et_2O, rt, 20 min; (b) **15** (0.25 equiv.), CH_2Cl_2, 50°C, 2.5 h; (iv) (a) 1.6 M *n*-BuLi (1.2 equiv.), THF, rt, 10 min, 50°C, 10 min; (b) **12**, **18** or **19** (1.2 equiv.), CH_2Cl_2, reflux, 2.5 h; (v) cat. I_2, toluene, reflux, 20 h.

Table 1. UV–vis absorptions μ_{eg}, $\mu_g(\mu_e-\mu_g)$, $\mu_g\beta$, $\mu_g\beta_0$ values for PNA and compounds **1**–**9**

Compound	λ_{max}[a] (nm)	λ_{cutoff}[b] (nm)	μ_{eg} (Debye)	$\mu_g(\mu_e-\mu_g)$ (Debye^2)	$\mu_g\beta$[c] (10^{-48} esu$^2 \cdot$ cm)	$\mu_g\beta_0$ (10^{-48} esu$^2 \cdot$ cm)	T_d[d] (°C)
1a	347	426	5.6	69	195	100	316
1b	337	406	5.6	47	118	63	278
2a	366	421	4.3	65	130	60	351
2b	364	412	4.6	43	98	46	277
3a	370	480	5.8	82	314	143	282
3b	368	469	4.6	57	135	62	210
4a	354	449	3.6	59	74	37	253
4b	351	466	4.4	30	53	27	192
5a[e]	403	465	–	–	590	219	311
5b[e]	393	453	–	–	488	195	288
6a[f]	385	448	6.0	51	243	101	–
7a[f]	450	518	7.8	66	1364	312	278
8a[f]	435	507	5.7	46	395	108	–
9a[g]	394	470	6.5	55	119	46	300
9b[g]	387	470	6.3	51	94	38	252
PNA	352	–	4.7	54	110	55	–

[a] Measured in dioxane.

[b] The wavelength where the absorbance is 5% of that at the λ_{max}.

[c] Estimated for a fundamental wavelength of 1064 nm.

[d] Heating rate of 10°C/min, heating range of 50–500°C.

[e] Ref. 7.

[f] Ref. 8.

[g] Ref. 9.

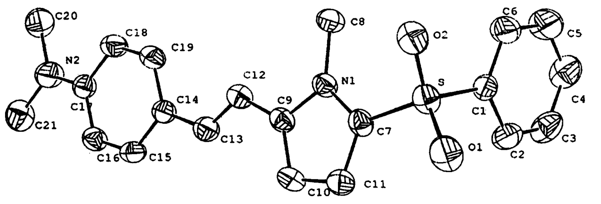


Figure 1. X-Ray crystal structure of **2a**.

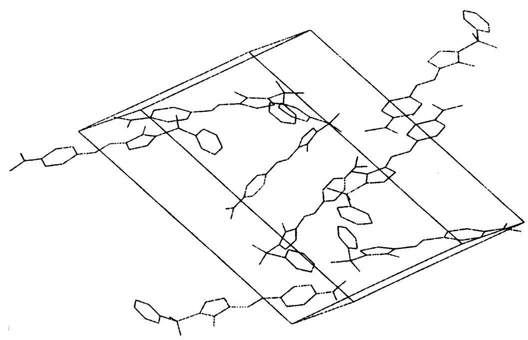


Figure 2. Packing drawing of compound **2a**.

The molecular hyperpolarizabilities ($\mu_g\beta$) of chromophores **1**–**4** were estimated by solvatochromism.[14] The $\mu_g\beta$ values at zero-frequency ($\mu_g\beta_0$) were obtained using the two-level model.[15] The $\mu_g\beta_0$ for compounds **1**–**4** are 0.5–2.6 times that of *p*-nitroaniline (PNA). By comparing the $\mu_g\beta_0$ values of **2a**, **5a**, **6a**; **3a**, **7a**, **8a** and **4a**, **9a**, **10a**, it can be seen that thiophene>furan>pyrrole, which is in agreement with the theoretical calculations.[16] Comparison of the $\mu_g\beta_0$ values of **1**–**9** reveals that replacing the methyl sulfone group with the phenyl sulfone group increases their second-order nonlinearities. Pyrrole compounds with a π-bridge of C=C have higher $\mu_g\beta_0$ values than the C=N analogues (**2a**/**9a**=1.3, **2b**/**9b**=1.2).

The decomposition temperatures (T_d) of **1**–**4** were measured by thermogravimetric analysis (TGA) at a heating rate of 10°C min^{-1}. It can be seen that the (phenyl)sulfonyl-substituted pyrrole chromophores have higher T_d than the (methyl)sulfonyl derivatives. The T_d shows a general trend of thiophene≈pyrrole (*N*-methylated)>furan. The T_d of compound **2a** (351°C) is among the highest we have observed for these heterocyclic compounds. Furthermore, within the pyrrole series, the T_d follows the order *trans*>*cis* and C=C>C=N.

We have also obtained the X-ray crystal structure of **2a** (Fig. 1)[17] which shows the *trans* configuration about the C=C bond and a dihedral angle of 4.53° between the benzene and the pyrrole ring. Compound **2a** has a noncentrosymmetric alignment with a $P2_12_12_1$ space group (Fig. 2).

In summary, we have achieved the first synthesis of a series of sulfonyl-substituted pyrrole chromophores **1**–**4** and have measured their UV–vis absorptions, second-order nonlinearities and decomposition temperatures. The $\mu_g\beta_0$ and T_d values of the pyrrole compounds are considerably improved by replacing the π-bridge of C=N with C=C. By comparing the thiophene, furan and pyrrole analogues it can be seen that the heterocyclic moiety has significant influence on the UV–vis absorptions, NLO properties and thermal stability.

Acknowledgements

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17. Crystal data for $C_{21}H_{22}N_2O_2S$ (**2a**): fw 366.47, orthorhombic, space group $P2_12_12_1$, $a=10.07(17)$ Å, $b=15.597(3)$ Å, $c=23.952(5)$ Å, $V=3763.0(12)$ Å^3, $Z=8$, $D_{calcd}=1.294$ g/cm^3, orange crystal (0.60×0.50×0.45 mm).