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Synthesis of Sulfone-Substituted Thiophene Chromophores for Second-Order Nonlinear Optics

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ABSTRACT: A new series of conjugated thiophene compounds **1-4** containing methylsulfonyl and phenylsulfonyl acceptors have been synthesized which possess efficient second-order optical nonlinearities, high thermal stability and good transparency for use as nonlinear optical materials.
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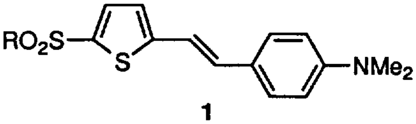
The design and synthesis of new donor-acceptor substituted conjugated compounds is presently a major focus of research in organic nonlinear optical (NLO) chromophores.[1-3] The sulfone group is a good acceptor substituent which is synthetically flexible and has broad transparency range in the visible spectrum, and benzene-based π-conjugated systems containing a sulfone group have been reported.[4] Recently, both molecular orbital calculations[5] and experimental studies[3] have revealed that the products of dipole moment and molecular hyperpolarizability (μβ) of thiophene-containing conjugated moieties are superior to benzene analogues. Based on the above reasons, we have studied previously the second-order nonlinearities of sulfone-substituted thiophene imino dyes.[6] In this communication we report the synthesis, UV-VIS absorption spectrum, thermal stability and second-order nonlinear optical properties of a series of new thiophene-containing chromophores **1-4** with methylsulfonyl and phenylsulfonyl acceptors.



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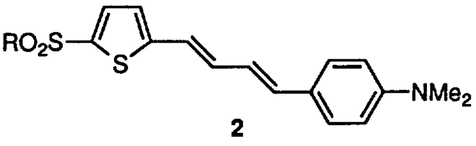

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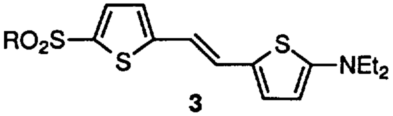

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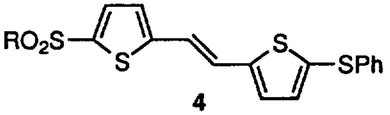

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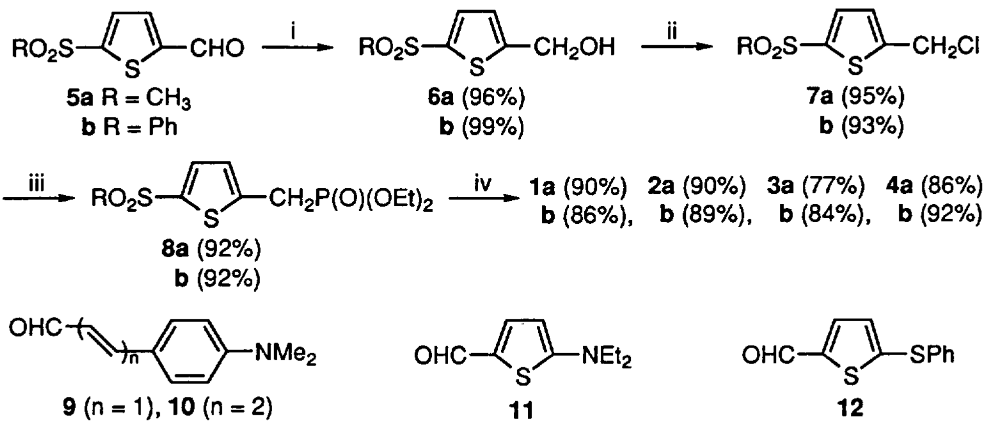
1-4: **a**, R = CH_3; **b**, R = Ph

The general methodology for the synthesis of these methylsulfone- and phenylsulfone-substituted thiophene-containing chromophores **1-4** is shown in Scheme 1. Reduction of compounds **5a**[6] and **5b**[6] with sodium borohydride gave **6a** (96%) and **6b** (99%) . Treatment of **6a** and **6b** with thionyl chloride gave the chloro compounds **7a** (95%) and **7b** (93%). Phosphonates **8a** (92%) and **8b** (92%) were obtained by reacting

7a and **7b** with triethyl phosphite. Thiophene-containing chromophores **1a-4a** and **1b-4b** were then obtained by a Wittig-Horner condensation reaction of phosphonates **8a** and **8b** with 4-*N*,*N*-dimethylaminobenzaldehyde **9**, 4-*N*,*N*-dimethylaminocinnamaldehyde **10**, 2-*N*,*N*-diethylamino-5-thiophenecarboxaldehyde **11** and 2-phenylthio-5- thiophenecarboxaldehyde **12**, respectively, in good yields.



Scheme 1 *Reagents and conditions*: i, $NaBH_4$, EtOH, 0 °C, 1 h; ii, $SOCl_2$, CH_2Cl_2, 25 °C, 24 h; iii, $(EtO)_3P$, 140 °C, 24 h; iv, NaH, **9** or **10** or **11** or **12** ,THF, 0 °C, 2 h.

The UV-VIS absorptions of compounds **1-4** were measured in 1,4-dioxane solvent (Table 1). It can be seen that compounds **1-4** have λ_{max} values below 450 nm, and have virtually no absorption at 532 nm as shown by their λ_{cutoff} values. These results also reveal that the phenylsulfones **1b-3b** have lower charge-transfer energy than the methylsulfones **1a-3a** for the strong donating amino group. Compounds **4a** and **4b** containing the weak donating methylthio or phenylthio group have absorption peaks at considerably shorter wavelength than the amino-substituted compounds **3a** and **3b**. Most importantly, compounds **1-4** show large blue shifts when compared to the corresponding nitro-,[7] dicyanovinyl-,[8] or tricyanovinyl-[9] substituted derivatives, e.g. 76 nm, 144 nm or 278 nm blue shift for methylsulfone **3a**, and 66 nm, 134 nm or 268 nm blue shift for phenylsulfone **3b**, respectively. The increased transparency of these sulfonyl compounds in the visible region should make them more suitable for use in second-harmonic generation (SHG) and other parametric processes in the visible spectrum.[4]

The $\mu\beta$ values of the sulfone-substituted thiophene chromophores were measured using the electric-field-induced second harmonic generation (EFISH) technique[10] at 1064 nm. Dioxane was used as the solvent, and the $\mu\beta$ values were calibrated against a reference solution of *p*-nitroaniline (PNA). The $\mu\beta$ of PNA was taken as 120×10^{-48} esu with crystalline quartz as the reference.[11] The zero-frequency $\mu\beta_0$ was corrected with a two-level model.[12] The Kurtz powder method[13] was used to determine the averaged SHG intensity using urea and quartz as the reference at 1064 nm.[14] The crystals of **1a-4a** and **1b-4b** were grown from a solution of dichloromethane and hexane by slow evaporation, and powders (75-150 μm) for SHG measurements were obtained by grinding these crystals. The results of EFISH and Kurtz powder test are listed in Table 1.

Table 1. UV-VIS absorptions, $\mu\beta$ values, $\mu\beta_0$ values, theoretical ground state dipole moment μ_g (AM1), theoretical $\mu\beta_0$ (AM1), powder SHG intensity and decomposition temperature (T_d) for PNA, and compounds **1-4**.

Compound	$\lambda_{max}{}^a$ / nm	$\lambda_{cutoff}{}^a$ / nm	$\mu\beta^b$ / 10^{-48}esu	$\mu\beta_0$ / 10^{-48}esu	μ_g (AM1) / Debye	$\mu\beta_0$ (AM1) / 10^{-48}esu	SHG intensity^b $[I(2\omega)_{sample}/I(2\omega)_{urea}]$	T_d / °C
1a	393	453	488	195	5.6	114	0.6	288
1b	403	465	590	219	7.0	182	7.1	311
2a	413	479	976	337	5.9	173	0.9	293
2b	420	491	1446	466	—	—	0.01^c	311
3a	440	508	1036	273	6.5	189	2.1	280
3b	450	518	2169	507	—	—	5.5	278
4a	366	423	28	13	—	—	0.002^c	312
4b	364	426	14	7	—	—	5.7	349
PNA	352	—	120	60	7.3	40	—	—

^{a} Measured in dioxane. ^{b} Measured with a fundamental wavelength of 1064 nm. ^{c} Measured with quartz as the reference, and then converted to the urea reference.[14]

Compounds **1a-3a** and **1b-3b** have large $\mu\beta$ and $\mu\beta_0$ values. The $\mu\beta$ values are 4.1-18 times that of PNA, whereas the $\mu\beta_0$ values are 3.3-8.5 times that of PNA. However, compounds **4a** and **4b** containing the weak donating phenylthio or methylthio group have rather small $\mu\beta$ and $\mu\beta_0$ values. Comparing the $\mu\beta$ values of **1a-3a** with those of **1b-3b**, it is clear that the phenylsulfonyl group is more effective than the methylsulfonyl group in directing the molecular nonlinearity. This is consistent with the fact that phenylsulfones have higher λ_{max} values than those of methylsulfones (Table 1). Extending the conjugation length in **1a** and **1b** with an ethylenic moiety led to **2a** and **2b** which showed significant enhancement of the second-order nonlinearity ($\mu\beta$ values: **2a**/**1a** = 2, **2b**/**1b** = 2.5; $\mu\beta_0$ values: **2a**/**1a** = 1.7, **2b**/**1b** = 2.1). However, the red shift caused by extending the ethylenic unit is only 10 nm and 17 nm for **2a** and **2b**, respectively. Comparison of **1a** and **1b** with **3a** and **3b** reveals that replacement of the benzene ring with the second thiophene structure markedly increases its nonlinearity ($\mu\beta$ values: **3a**/**1a** = 2.1, **3b**/**1b** = 3.7; $\mu\beta_0$ values: **3a**/**1a** = 1.4, **3b**/**1b** = 2.3). The theoretical ground state dipole moment μ_g and zero-frequency hyperpolarizability $\mu\beta_0$ of some of the molecules were also calculated by a gas-phase geometry optimization of the AM1 parameterization of MOPAC[15] for comparison (Table 1). It can be seen that the calculations are in reasonably good agreement with the experimental results. It is interesting to point that, though the absorption maximum of **1a** and **1b** shifts to shorter wavelength than that of the corresponding imino derivatives,[6] the $\mu\beta$ values of **1a** and **1b** increase compared with those imino derivatives. This could be due to greater change in dipole moment between the ground and first excited state ($\Delta\mu_{eg}$) for the C=C than C=N linkage.[12] Furthermore, four out of the eight compounds that we have synthesized show larger averaged SHG intensities than that of urea by the powder measurement at 1064 nm. Such a high proportion (50%) of active materials is not often encountered in the screening of organic crystalline powders for second-order nonlinear optical materials.[14]

The thermal stability of these sulfone-substituted thiophene chromophores was determined by thermogravimetric analysis (TGA). All samples showed very high decomposition temperatures (T_d) at a heating rate of 10 °C min^{-1} (Table 1). The onset of thermal decomposition was obtained by the intercept of the leading edge of weight loss with the base line. Generally, the thermal stability of phenylsulfone compounds **1b** (311 °C), **2b** (311 °C) and **4b** (349 °C) is greater than that of methylsulfone compounds **1a** (288 °C), **2a** (293 °C) and **4a** (312 °C), with the exception for compounds **3b** (278 °C) and **3a** (280 °C). The high thermal stability of these sulfone-substituted chromophores is very important for use in nonlinear optics.

In conclusion, we have synthesized a series of methylsulfone- and phenylsulfone-substituted thiophene chromophores which show efficient second-order optical nonlinearities, high thermal stability and good transparency in the visible region. These compounds should be quite useful for NLO applications.

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