

Second-order nonlinearities and crystal structures of methylsulfonyl- and phenylsulfonyl-substituted thiophene imino dyes

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A simple synthesis of sulfone-substituted thiophene imino dyes 5 and 6 and their UV–VIS absorptions, second-order nonlinear optical properties, X-ray crystal structures and thermal stabilities are described.

Organic materials have been demonstrated in recent years to possess many superior second-order nonlinear (NLO) properties as compared to inorganic materials.^{1–4} The NLO materials have great potential for use in optical communications, information processing, frequency doubling and integrated optics.^{3,4} Recently, both molecular orbital calculations⁵ and experimental studies⁶ have revealed that molecular hyperpolarizabilities ($\mu\beta$) of thiophene-containing conjugated moieties are greater than benzene analogues. However, to achieve the required noncentrosymmetric order has been a major obstacle because the majority of organic compounds crystallize in centrosymmetric space groups.² Here we report the synthesis and NLO properties of two new thiophene imino dyes **5** and **6** containing sulfonyl acceptors. Although the sulfonyl group is not as strong an electron-withdrawing group as the nitro, di- or tri-cyanoethenyl group, it is synthetically more flexible and has greater transparency in the visible spectrum.⁷

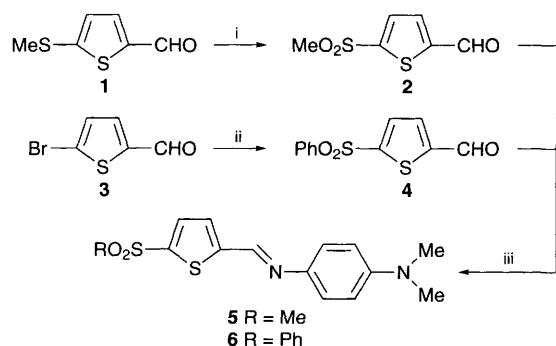
The synthesis of imino dyes **5** and **6** is shown in Scheme 1. Oxidation of 5-(methylsulfonyl)thiophene-2-carboxaldehyde **1** (Maybridge) with MCPBA gave the corresponding methylsulfonyl **2**. The phenylsulfonyl **4** was prepared from **3** by a literature method.⁸ Condensation of compounds **2** and **4** with

4-*N,N*-dimethylaminoaniline gave the imino dyes **5** and **6** respectively in good yields.[†]

The UV–VIS absorptions of the imino dyes **5** and **6** were measured in different solvents[‡] and the results reveal that the phenylsulfonyl **6** has lower charge-transfer energy and higher solvatochromic effect than the methylsulfonyl **5**. However, both these compounds show a large blue shift compared to the nitro-substituted thiophene imino dye **7**: 72 nm for **5** and 63 nm for **6** in CH_2Cl_2 . The greater transparency of **5** and **6** should make them more suitable for generating blue–green laser lights by the frequency-doubling technique.

The molecular hyperpolarizabilities ($\mu\beta$) of the imino dyes **5** and **6** were measured using the electric-field-induced second harmonic generation (EFISH)⁹ technique 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.¹⁰ The zero-frequency hyperpolarizability ($\mu\beta_0$) was calculated using a two-level model.¹¹ The Kurtz powder method was used to determine the averaged second harmonic generation (SHG) intensity using urea and α -quartz as the reference.¹² Large single crystals of **5** and **6** were grown from a solution of ethanol 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.

The $\mu\beta$ values of **5** and **6** are 3.0 and 3.8 times that of PNA, whereas the $\mu\beta_0$ are 1.9 and 2.3 times that of PNA, respectively.



Scheme 1 Reagents and conditions: i, MCPBA, CH_2Cl_2 , 0–25 °C, 2 h; ii, PhSO_2Na , DMF, 130 °C, 3 h; iii, 4-*N,N*-dimethylaminoaniline, 4 Å molecular sieve, CH_2Cl_2 , 25 °C, 2 h

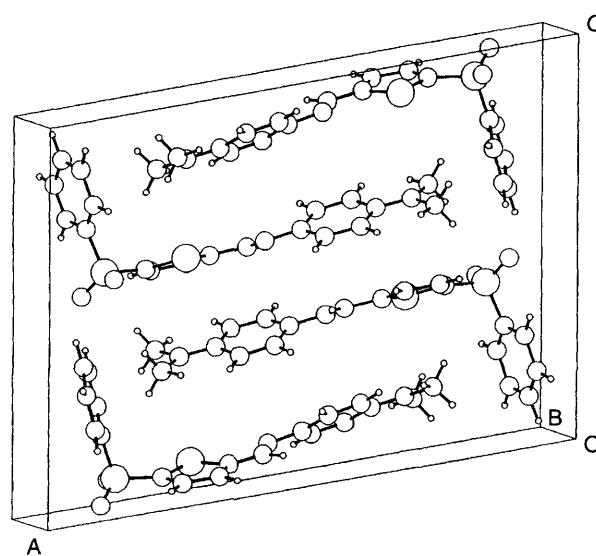
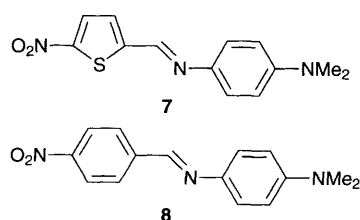
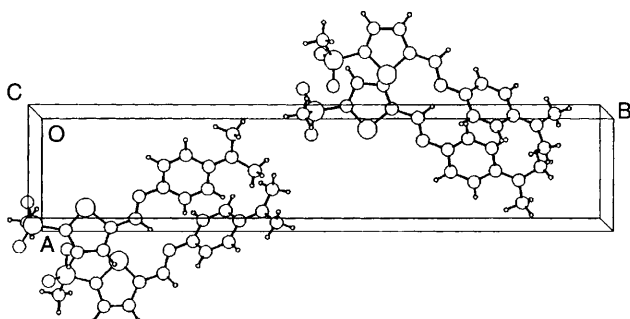


Fig. 1 Packing drawing of compound **6** (space group $P2_1/c$)

Table 1 UV–VIS, melting point, decomposition temperature, $\mu\beta$ values, $\mu\beta_0$ values and powder SHG intensity for PNA and compound 5–8

Compound	λ_{\max}/nm	$T_m/\text{°C}$	$T_d/\text{°C}$	$\mu\beta/10^{-48}\text{ esu}$	$\mu\beta_0/10^{-48}\text{ esu}$	SHG intensity $[I(2\omega)_{\text{sample}}/I(2\omega)_{\text{urea}}]$
PNA	352 ^a	146	—	120 ^{a,b}	60	—
5	422 ^a	174	295	361 ^{a,b}	113	13
6	429 ^a	210	286	458 ^{a,b}	135	5×10^{-3}
7 ^c	503 ^d	—	—	807 ^{d,e}	431	—
8 ^c	458 ^f	—	—	500 ^{f,g}	241	1–3 ^h

^a Measured in dioxane. ^b Measured with a fundamental wavelength of 1064 nm. ^c Ref. 13. ^d Measured in methylene chloride. ^e Measured with a fundamental wavelength of 1579 nm. ^f Measured in Me₂SO. ^g Measured with a fundamental wavelength of 1356 nm. ^h Ref. 14.

**Fig. 2** Packing drawing of compound 5 (space group $P2_1$)

This shows that the imino dyes 5 and 6 have reasonably high hyperpolarizabilities and that the phenylsulfonyl group in 6 has a larger effect than the methylsulfonyl group in 5. In consistence with the UV–VIS data, the $\mu\beta$ and $\mu\beta_0$ values of 5 and 6 are slightly lower than those of the nitrothiophene compound 7 and nitrobenzene compound 8.¹³ The SHG intensity of methylsulfone 5 is 13 times higher than that of urea, and 4–13 times higher than nitrobenzene 8 (1–3 times of urea).¹⁴ The averaged SHG intensity of phenylsulfone 6 is only 5×10^{-3} that of urea. Thus, the SHG intensity ratio of 5:6 is 2.6×10^3 .

To explain the above unexpected SHG results, the single crystal X-ray structures of 5 and 6 were obtained (Figs. 1 and 2). Both compounds have the *E* configuration about the C–N bond. The phenylsulfone 6 has a centrosymmetric alignment with $P2_1/c$ space group (four molecules per unit cell), whereas the methylsulfone 5 is noncentrosymmetric with a $P2_1$ space group. § The substantial structural difference caused by the two sulfone groups of the imino dyes 5 and 6 has led to completely different crystal alignments and second-order nonlinearities. Apparently the much larger phenylsulfonyl group in 6 makes a head-to-tail arrangement of the molecule impossible. We can now obtain $15 \times 4 \times 1$ mm single crystals of 5 from a solution of ethanol and hexane by slow evaporation.

The melting points (T_m) of 5 and 6 are 174 and 210 °C, respectively as measured by differential scanning calorimetry (DSC) at a heating rate of 10 °C min^{-1} . The decomposition temperatures (T_d) of 5 and 6 are 295 and 286 °C, respectively as determined by thermogravimetric analysis (TGA) at a heating rate of 10 °C min^{-1} . It is interesting to note that the phenylsulfonyl-substituted thiophene imino dye 6 has lower T_d than the methylsulfone derivative 5. High melting and decomposition temperatures of organic crystals are very important for NLO applications.²

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Footnotes

† All new compounds gave satisfactory spectral and analytical data.

‡ λ_{\max}/nm for 5: 431 (Me₂SO), 431 (CH₂Cl₂), 428 (DMF), 425 (MeOH), 422 (dioxane), 415 (hexane). For 6: 446 (Me₂SO), 440 (CH₂Cl₂), 439 (DMF), 433 (MeOH), 429 (dioxane) and 420 (hexane).

§ Crystal data for 5: C₁₄H₁₆N₂O₂S₂, $M = 308.4$, monoclinic, space group $P2_1$, $a = 6.012(3)$, $b = 30.644(9)$, $c = 8.163(4)$ Å, $\beta = 95.93(4)^\circ$, $V = 1495.6(11)$ Å³, $Z = 4$, $D_c = 1.370$ g cm⁻³, θ - 2θ scan type $14.50 \leq 2\theta \leq 27.56^\circ$, $F(000) = 649$, $\mu = 3.428$ cm⁻¹, $T = 298$ K, crystal size = $0.30 \times 0.30 \times 0.30$ mm. Of 2867 measured data 2678 were unique and 1875 were observed [$I > 2.0\sigma(I)$]. The structure was solved by direct methods and refined to give $R = 0.045$ and $R_w = 0.049$. For 6: C₁₉H₁₈N₂O₂S₂, $M = 370.48$, monoclinic, space group $P2_1/c$, $a = 20.038(7)$, $b = 6.1450(20)$, $c = 14.773(4)$ Å, $\beta = 99.25(3)^\circ$, $V = 1795.4(10)$ Å³, $Z = 4$, $D_c = 1.371$ g cm⁻³, θ - 2θ scan type $15.68 \leq 2\theta \leq 24.10^\circ$, $F(000) = 777$, $\mu = 2.977$ cm⁻¹, $T = 298$ K, crystal size = $0.20 \times 0.40 \times 0.70$ mm. Of 3144 measured data 3144 were unique and 1304 were observed [$I > 2.0\sigma(I)$]. The structure was solved by direct methods and refined to give $R = 0.047$ and $R_w = 0.046$. Atomic coordinates, thermal parameters and bond lengths have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *Chemical Communications*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/22.

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