

Arylthienyl-vinyl-benzothiazoles as Efficient Second Harmonic Generators (SHG) for Nonlinear Optics †

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Abstract: New push-pull second harmonic generation (SHG) chromophores **2** were synthesized in order to study their linear and nonlinear optical properties. The donor-acceptor π -conjugated systems **2** were prepared in good to excellent yields by a simple aldol-type condensation of the precursor aldehydes **1** with 6-nitro-2-methyl-1,3-benzothiazole in the presence of NaOH. Hyper-Rayleigh scattering in dioxane solutions was used to evaluate their second-order nonlinear optical properties. The experimental results showed that the optical (linear and nonlinear) properties are influenced by the electron-donor strength of the groups of the π -conjugated bridge. The vinyl-benzothiazole derivative **2b**, with methoxyl as the donor group, exhibited the largest first hyperpolarizability β (1660×10^{-30} esu, 40 times greater than the standard reference *p*NA molecule) and the highest decomposition temperature ($T_d = 360$ °C). The good balance between nonlinearity and thermal stability makes this compound a promising candidate as second harmonic generator (SHG) for nonlinear optics.

Keywords: synthesis; benzothiazole; thiophene; thermal stability; second harmonic generators (SHG)

1. Introduction

Organic molecules comprising strong electron donor and acceptor groups connected by a π -conjugated system (often designated as donor- π -acceptor or “push-pull” chromophores) are of fundamental importance in materials chemistry due to their numerous applications in modern technology, such as nonlinear optical (NLO) devices, poled polymers, photovoltaic cells, organic light-emitting diodes (OLEDs), semiconductor materials, and optical data storage devices [1–4]. Several push-pull molecules containing benzothiazole as an (auxiliary) electron-withdrawing group have already been reported, and typically exhibit favorable fluorescence, electrochemical, solvatochromic, photochromic, and NLO properties [5–7]. We have reported the synthesis and characterization of the UV-vis, solvatochromic, thermal, and second-order NLO properties of benzothiazole derivatives containing bithienyl [8–9], arylthienyl [10], and thienylpyrrolyl [11–12] heterocyclic π -spacers in order to evaluate the effect of different π -excessive donor moieties/ π -bridges on their optical properties. As an extension of our earlier work and in order to improve the thermal stability and NLO properties of heterocyclic chromophores of the benzothiazole type, we decided to synthesize arylthienyl-benzothiazoles bearing a vinyl spacer between the donor π -excessive heterocycle (thiophene) and the acceptor π -deficient benzothiazole moiety. In this work,

we report the synthesis and characterization of the optical and thermal properties of two vinyl-benzothiazole derivatives as second harmonic generators (SHG) for NLO applications.

2. Materials and Methods

2.1. General

The reaction progress was monitored by thin layer chromatography (0.25 mm thick precoated silica plates: Merck Fertigplatten Kieselgel 60 F254), while purification was carried out by silica gel column chromatography (Merck Kieselgel 60; 230–400 mesh). NMR spectra were obtained on a Varian Unity Plus Spectrometer at an operating frequency of 300 MHz for ^1H NMR and 75.4 MHz for ^{13}C NMR using the solvent peak as the internal reference. The solvents are indicated in parentheses before the chemical shift values (δ relative to TMS and given in ppm). Mps were determined on a Gallenkamp apparatus and are uncorrected. Infrared spectra were recorded on a BOMEM MB 104 spectrophotometer. UV-vis absorption spectra (200–800 nm) were obtained using a Shimadzu UV/2501PC spectrophotometer. Mass spectrometry analyses were performed at the “C.A.C.T.I.—Unidad de Espectrometria de Masas” at the University of Vigo, Spain. Thermogravimetric analysis of samples was carried out using a TGA instrument model Q500 from TA Instruments. 5-Phenylthiophene-2-carbaldehyde **1a** and 5-(4-methoxyphenyl)thiophene-2-carbaldehyde **1b** used as precursors for the synthesis of compounds **2** were purchased from Aldrich and Acros and used as received. The synthesis of 6-nitro-2-methyl-1,3-benzothiazole has been reported previously and is commercially available (CAS 2941-63-1). Nevertheless, in our work, it was prepared from the corresponding 2-methyl-1,3-benzothiazole following the literature procedure [13].

2.2. General Procedure For the Synthesis of Compounds **2**

To a solution of 6-nitro-2-methylbenzothiazole (0.20 mmol) and arylthienyl-aldehydes **1** (0.20 mmol) in ethanol (5 mL), a solution of NaOH (0.30 mmol) dissolved in a minimum amount of water was added dropwise. The reaction mixture was left stirring at room temperature for 3–5 h and the resulting precipitate was collected and purified by recrystallization from ethanol.

6-Nitro-2-[(E)-2-(2'-phenylthienyl)vinyl]-1,3-benzothiazole (2a). Orange solid (70%). Mp: 221.0–222.0 °C. UV (1,4-dioxane): λ_{max} nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 415.0 (18,165). IR (Nujol) ν 3109, 1777 (C=C), 1607, 1566, 1515, 1333, 1286, 1223, 1131, 1100, 1064, 946, 919, 892, 834, 758 cm^{-1} . ^1H NMR (DMSO- d_6) δ 7.33 (d, 1H, $J_{(\text{trans})}$ = 15.6 Hz, =CH), 7.35–7.36 (m, 1H, H-4''), 7.43–7.47 (m, 2H, H-3'' and H-5''), 7.55 (d, 1H, J = 4.0 Hz, H-3'), 7.59 (d, 1H, J = 4.0 Hz, H-4'), 7.71 (d, 2H, J = 7.2 and 1.6 Hz, H-2'' and H-6''), 7.98 (d, 1H, $J_{(\text{trans})}$ = 16 Hz, =CH), 8.09 (d, 1H, J = 8.8 Hz, H-4), 8.30 (dd, 1H, J = 8.8 and 2.4 Hz, H-5), 9.07 (d, 1H, J = 2.4 Hz, H-7). ^{13}C NMR (DMSO- d_6) δ 118.64 (C-7), 119.31 (=CH), 121.47 (C-5), 122.15 (C-4), 124.74 (C-3'), 125.29 (C-2'' and C-6''), 128.11 (C-4''), 128.84 (C-3'' and C-5''), 132.04 (=CH), 132.32 (C-4'), 132.79 (C-1''), 134.61 (C-7a), 138.83 (C-5'), 144.02 (C-6), 146.11 (C-2'), 157.08 (C-3a), 171.74 (C-2). MS (FAB) m/z (%): 365 ([M + H] $^+$, 28), 307 (35), 289 (16), 155 (37), 154 (100). HRMS: (FAB) m/z (%) for $\text{C}_{19}\text{H}_{12}\text{N}_2\text{O}_2\text{S}_2$; calcd 365.0418; found 365.0424.

6-Nitro-2-[(E)-2-(2'-(4''-methoxyphenyl)thienyl)vinyl]-1,3-benzothiazole (2b). Orange solid (80%). Mp: 205.0–206.0 °C. UV (1,4-dioxane): λ_{max} nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 430.0 (14,055). IR (Nujol) ν 1671 (C=C), 1616, 1604, 1592, 1507, 1335, 1248, 1178, 1127, 1027, 946, 833, 809, 754, 720 cm^{-1} . ^1H NMR (DMSO- d_6) δ 3.81 (s, 3H, OCH $_3$), 7.00 (d, 2H, J = 6.8 and 2.0 Hz, H-3'' and H-5''), 7.26 (d, 1H, $J_{(\text{trans})}$ = 15.6 Hz, =CH), 7.42 (d, 1H, J = 4.0 Hz, H-3'), 7.54 (d, 1H, J = 4.0 Hz, H-4'), 7.63 (dd, 2H, J = 6.8 and 2.0 Hz, H-2'' and H-6''), 7.96 (d, 1H, $J_{(\text{trans})}$ = 16 Hz, =CH), 8.07 (d, 1H, J = 9.2 Hz, H-4), 8.28 (dd, 1H, J = 8.8 and 2.4 Hz, H-5), 9.05 (d, 1H, J = 2.4 Hz, H-7). ^{13}C NMR (DMSO- d_6) δ 55.04 (OCH $_3$), 114.46 (C-3'' and C-5''), 118.59 (C-7), 118.67 (=CH), 121.45 (C-5), 122.05 (C-4), 123.53 (C-3'), 125.53 (C-1''), 126.74 (C-2'' and C-6''), 132.21 (=CH), 132.56 (C-4'), 134.55 (C-7a), 137.74 (C-5'), 143.95 (C-3a), 146.42 (C-2'), 157.12 (C-6), 159.47 (C-4''), 171.84 (C-2). MS (FAB) m/z (%): 395 ([M + H] $^+$, 37), 307 (41), 289 (19), 155 (32), 154 (100). HRMS: (FAB) m/z (%) for $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_3\text{S}_2$; calcd 395.0524; found 395.0536.

2.3. Nonlinear Optical Measurements Using the Hyper-Rayleigh Scattering (HRS) Method [14]

The hyper-Rayleigh scattering (HRS) technique was used to measure the angle averaged first hyperpolarizability β of the molecules studied. The experimental set-up for hyper-Rayleigh measurements employed a q-switched Nd:YAG laser and is similar to the one presented by Clays and Persoons [14–15]. Details of the experimental procedure used have been previously published [11]. We emphasize that particular care was taken to avoid reporting artificially high first hyperpolarizabilities by using a pair of interference filters to estimate and correct for the presence of a possible contamination of the hyper-Rayleigh signal by molecular fluorescence near 532 nm. Further cautions include normalizing the hyper-Rayleigh signal at each pulse using the second harmonic signal from a 1 mm quartz plate to compensate for fluctuations in the temporal profile of the laser pulses due to longitudinal mode beating and filtering of the solutions, using a 0.2 mm porosity filter, to avoid spurious signals from suspended impurities. Dioxane was used as a solvent for all measurements. To calibrate our system, a reference solution of *p*-nitroaniline (*p*NA) [16–17] dissolved in dioxane at a concentration of 1×10^{-2} mol dm⁻³ (external reference method) was used. The hyperpolarizability of *p*NA dissolved in dioxane is known from EFISH measurements carried out at the same fundamental wavelength [16–17]. All solutions were filtered (0.2 mm porosity) to avoid spurious signals from suspended impurities. The small hyper Rayleigh signal that arises from dioxane was taken into account. Kaatz and Shelton [18] have measured the value of β_{333} of *p*NA in dioxane at 1064 nm to be 40×10^{-30} esu using the so-called Taylor convention for the first hyperpolarizability [19]. This value has been corrected by a factor of 1.88 for the most recent calibration factor of the hyper-Rayleigh scattering signal of CCl₄, which was used as a reference [20].

2.4. Thermogravimetric Analysis of Benzothiazoles 2

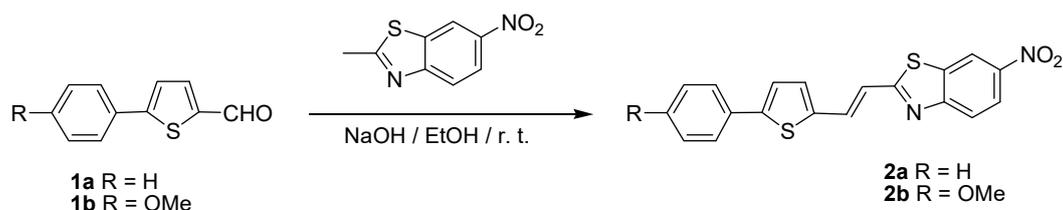
Thermogravimetric analysis of samples was carried out using a TGA instrument model Q500 from TA Instruments, under high purity nitrogen supplied at a constant 50 mL min⁻¹ flow rate. All samples were subjected to a 20 °C min⁻¹ heating rate and were characterized between 25 and 800 °C.

3. Results and Discussion

3.1. Synthesis

Benzothiazoles **2** with arylthienyl π -bridges were obtained in good yields (70–80%) by the condensation of 6-nitro-2-methyl-1,3-benzothiazole with formyl derivatives **1a–b** in ethanol, in the presence of aqueous sodium hydroxide solution, at room temperature for 3–5 h (Scheme 1, Table 1). In our work, the 2-methyl-1,3-benzothiazole precursor was functionalized with a nitro withdrawing group at position 6, which promoted great advantages: (i) increase the acidity of methyl protons at position 2, which afford minor reaction times and better yields; and (ii) the reaction products obtained were vinyl products in the absence of aldol intermediates, without heating the reaction mixture. 6-Nitro-2-methyl-1,3-benzothiazole has been reported previously and is commercially available. It was easily prepared in 84% yield by the nitration of 2-methyl-1,3-benzothiazole using a mixture of nitric acid/sulfuric acid (3:1) as nitration agents [13] in sulfuric acid at 2–3 °C for 30 min.

The ¹H NMR and ¹³C NMR data of vinyl-benzothiazole derivatives **2** were consistent with the designed structures. In the ¹H NMR spectra, signals at about 7.26–7.33 ppm and 7.96–7.98 ppm were detected. All signals appeared as duplets, with a *J*(H,H) coupling constants range of 16.0 Hz, and were attributed to the vinylic protons (CH=CH). These coupling constants clearly confirm the selective formation of *trans*-configured double bonds. A strong correlation could be observed between the π -bridge donor properties and the chemical shift of the vinylic protons in compounds **2** (Table 1). In fact, the increase of the donor ability of the attached group at the donor end of the π -conjugated bridge (the comparison between compound **2a**, R=H, δ = 7.33 ppm and compound **2b**, R=OMe, δ = 7.26 ppm) decreased the chemical shift of the vinylic protons. In the IR spectra of compounds **2**, the vinylic =CH was identified as a sharp band within the spectral region of 1671–1777 cm⁻¹.



Scheme 1. Synthesis of arylthienyl-vinyl-benzothiazoles **2**.

Table 1. Yields, IR, UV-visible absorption, and ^1H NMR data of arylthienyl-vinyl-benzothiazoles **2**.

Benzothiazole	R	Yield (%)	IR ν (cm^{-1}) ^a	δ_{H} (ppm) ^b	UV-Vis	
					λ_{max} (nm) ^c	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)
2a	H	70	1777	7.33; 7.98	415	18,165
2b	OMe	80	1671	7.26; 7.96	430	14,055

^a For the CH=CH stretching band for compounds **2** (recorded in Nujol). ^b For the CH=CH proton of the vinyl moiety for compounds **2** (DMSO- d_6). ^c All the UV-vis spectra were recorded in dioxane (10^{-4} M solution).

3.2. Photophysical Study of Benzothiazoles **2**

The absorption and emission spectra of arylthienyl-vinyl-benzothiazoles **2** were measured in dioxane (10^{-4} M solution) (Tables 1 and 2, Figure 1). The absorption spectra of benzothiazoles **2** showed an intense lowest energy charge-transfer band with high extinction coefficients in the UV-visible region. The position of this band was influenced by the electronic nature of the donor ability of the attached group at the donor end of the π -conjugated bridge. This can be seen comparing the absorption data for compounds **2b** ($\lambda_{\text{max}} = 430$ nm) and **2a** ($\lambda_{\text{max}} = 415$ nm), in which the replacement of the proton by a stronger donor group as methoxyl induced a bathochromic shift. The same behavior was observed in the emission spectra, with a bathochromic shift at about 30 nm for compound **2b** in comparison to the unsubstituted **2a**. Large Stokes' shifts were observed for chromophores **2**, as a consequence of intramolecular charge transfer from the donor to the acceptor moieties after excitation by light. The large Stokes' shift is indicative of a large difference in the spatial arrangement of the chromophore in the absorbing and emitting states, with a consequent increase in the dipole moment and orientational polarizability [21–22].

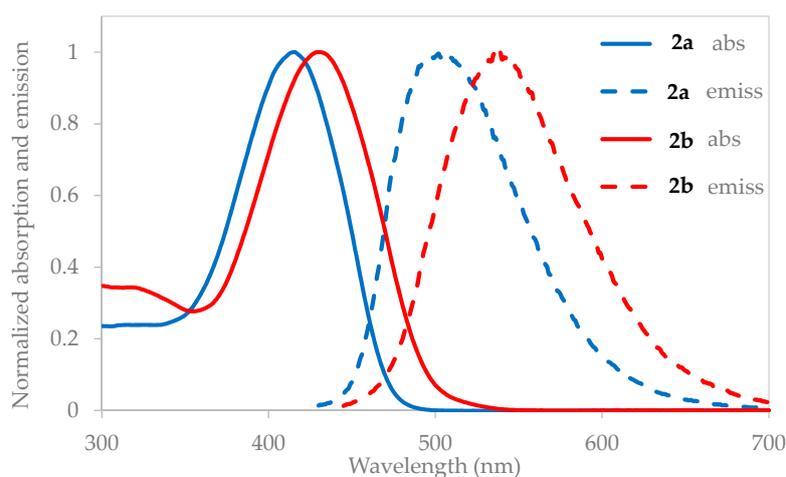


Figure 1. Normalized UV-vis absorption and emission spectra of compounds **2a** and **2b** in dioxane at $T = 298$ K (**2a**, $\lambda_{\text{exc}} = 415$ nm; **2b**, $\lambda_{\text{exc}} = 430$ nm) (absorption, full line; emission, dashed line).

Table 2. UV-vis and emission data, β and β_0 values and T_d data for arylthienyl-vinyl-benzothiazoles **2** ^a.

Benzothiazole	R	UV-Vis	Emission		$\beta/10^{-30}$ (esu) ^b	$\beta_0/10^{-30}$ (esu) ^c	T_d (°C) ^d
		λ_{\max} (nm) ^a	λ_{em} (nm) ^a	Stokes' Shift (cm ⁻¹)			
2a	H	415	506	4333	273	91	356
2b	OMe	430	537	4633	1660	482	360
<i>p</i> NA	—	352	—	—	40 [18–19]	20	—

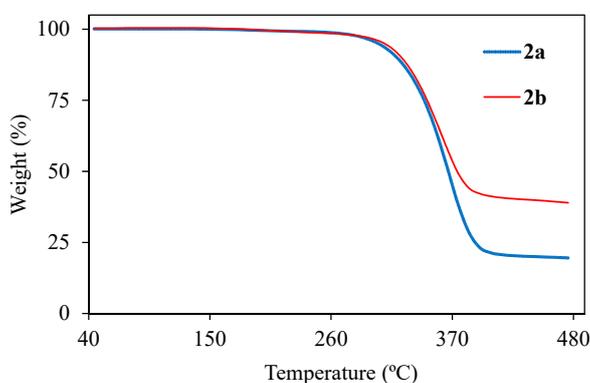
^a Experimental hyperpolarizabilities and spectroscopic data measured in dioxane solutions. ^b All the compounds are transparent at the 1064 nm fundamental wavelength. Values are reported in the T convention assuming that a single longitudinal element dominates the hyperpolarizability tensor. Estimated uncertainties are 10% of the reported values. ^c Data corrected for resonance enhancement at 532 nm using the two-level model with $\beta_0 = \beta [1 - (\lambda_{\max}/1064)^2][1 - (\lambda_{\max}/532)^2]$; damping factors not included 1064 nm [23, 24, 25, 26]. ^d Decomposition temperature (T_d) measured at a heating rate of 20 °C min⁻¹ under a nitrogen atmosphere, obtained by TGA.

3.3. Non-Linear Optical Properties and Thermal Stability of Benzothiazoles **2**

We have used the hyper-Rayleigh scattering (HRS) method [14–15] to measure the first hyperpolarizability β of benzothiazoles **2** using the 1064 nm fundamental wavelength of a Q-switched Nd:YAG laser. Dioxane was used as the solvent, and the β values were measured against a reference solution of *p*-nitroaniline (*p*NA) [16–17] in order to obtain quantitative values, while care was taken to properly account for possible fluorescence of the chromophores. The static hyperpolarizability β_0 values were calculated using the simple two-level model neglecting damping, as proposed by Oudar and Chemla [23–26]. They are therefore only indicative and should be treated with caution (Table 2).

From Table 2, it is observed that the increase of the electron donor strength of the group at the donor end of the arylthienyl π -conjugated bridge, resulted in both red-shifted absorption maxima and an enhanced β value for benzothiazole **2b** (R=OMe, $\lambda_{\max} = 430.0$ nm, $\beta = 1660 \times 10^{-30}$ esu), compared to derivative **2a** (R=H, $\lambda_{\max} = 415.0$ nm, $\beta = 273 \times 10^{-30}$ esu). In general, the values of the molecular hyperpolarizability β for benzothiazoles **2** were 7–40 times greater than that of *p*NA, whereas the β_0 values were 4–24 times higher than that of *p*NA, respectively. These NLO-phores **2** were specially designed to obtain exceptionally large β values. The introduction of a nitro withdrawing group (acting as acceptor part) bound to the benzothiazole auxiliary acceptor moiety promoted an improvement in the acceptor ability and, consequently, enhanced the charge transfer properties.

The thermal stability of chromophores **2** was estimated by thermogravimetric analysis (Table 2). As may be observed, the thermogravimetric curves exhibited only one-step weight loss processes with high decomposition temperatures, measured at a heating rate of 20 °C min⁻¹ under nitrogen. The most stable compound was benzothiazole **2b** ($T_d = 360$ °C) (see Figure 2).

**Figure 2.** Thermogravimetric curves of compounds **2a** and **2b**. Temperature gradient: 20 °C min⁻¹ under nitrogen.

The comparison of β and T_d values indicates that the nonlinearity and thermal stability are well-adjusted for these compounds, particularly for compound **2b**, which possesses both the highest β value (1660×10^{-30} esu, 40 times greater than *p*NA) and the highest decomposition temperature ($T_d = 360$ °C) (Table 2, Figure 2).

4. Conclusions

We have synthesized new benzothiazoles **2** in good yields by a simple procedure and their optical properties were evaluated. The donor-acceptor π -conjugated benzothiazoles **2** functionalized by groups with different electronic characters, have been evaluated and it was proved that the electronic nature of these groups had a significant influence on the SHG properties. In particular, we have shown that chromophore **2b** had a high molecular nonlinearity, as its β value was 40 times greater than that of the well-known *p*NA molecule. Compounds **2** exhibited excellent nonlinearities and high thermal stabilities making them appropriate candidates as push-pull second harmonic generators (SHG) for NLO applications.

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