

# SYNTHESIS AND CHEMICAL-OPTICAL CHARACTERIZATION OF *PUSH-PULL* STILBENES

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*This paper is dedicated to Professor Pedro Joseph-Nathan in recognition of his 50 years of outstanding scientific trajectory.*

## ABSTRACT

In this work we report the synthesis and spectroscopic characterization of *push pull* stilbenes. These compounds were prepared in good yield and characterized by <sup>1</sup>H and <sup>13</sup>C NMR, IR and MS. Single-crystal X-ray diffraction analysis of acids **1** and **2** evidenced the existence of intermolecular hydrogen bonding which in the case of compound **1** [(*Z*)-isomer] involves interaction between the acid group and a methoxy group other neighbor molecule in contrast for in (*E*)-isomer (**2**) the intermolecular hydrogen bonding is between the acid groups promoting the formation of centrosymmetric dimmers. From acids **1** and **2** was obtained the ester **3**, for which was improved its solubility properties. Lineal and non linear optical characterization of ester derivative was carried out in particular the second molecular hyperpolarizability using the Maker-Fringe technique. [www.relaquim.com](http://www.relaquim.com)

**Keywords:** Stilbene, push-pull, nonlinear optics, NLO, X-ray diffraction.

## RESUMEN

En este trabajo se describe la síntesis y la caracterización espectroscópica de nuevos compuestos estilbenos tipo donador- $\pi$ -aceptor (*push-pull*). Dichos compuestos fueron obtenidos en buenos rendimientos y caracterizados por RMN de hidrógeno y carbono, la espectrometría de masa muestra el ion molecular y para el caso de los ácidos marcados como **1** y **2**, fue posible establecer su estructura mediante difracción de rayos-X. En ambos compuestos se encuentran presentes interacciones por puente de hidrógeno, para el caso del compuesto **1** (isómero *Z*) dicha interacción se da entre el grupo ácido y el grupo metoxilo, mientras que en el

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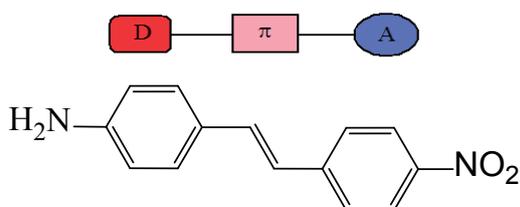
compuesto **2** (isómero *E*) el puente de hidrógeno intermolecular es entre los grupos ácidos. Finalmente para el éster **3**, fue posible medir la segunda hiperpolarizabilidad molecular mediante la técnica Maker-Fringe. [www.relaquim.com](http://www.relaquim.com)

**Palabras clave:** Estilbenos, donador- $\pi$ -aceptor (*push-pull*), óptica no lineal, ONL, difracción de rayos-X.

## INTRODUCTION

Nonlinear optical (NLO) properties were first observed in the decade of the sixties after the discovery of the laser by Franken *et al.* (1961), and certainly inorganic compounds have been the most studied and used in the manufacture of optoelectronic devices. However, in the last two decades organic nonlinear optical materials have been greatly investigated by Goto *et al.* (1991) due to their potentially high nonlinearities and rapid response in electro-optic effect compared to inorganic NLO materials. Moreover, these compounds are structurally modifiable and allow modulation of the NLO effect, in contrast to inorganic compounds where this is not possible. Also, organic compounds show other advantages over inorganic ones such as low-refractive index, their polarizabilities are purely and in particular they have lower processing cost.

It is well known that organic compounds that present NLO responses must contain into their molecular structure an electron donor and an acceptor group bonded by a conjugated  $\pi$  electron system. For this reason, the design of *push-pull* chromophores has been based on a dipolar D-p-A structural motif (Figure 1).



**Figure 1.** *Push-Pull* model

In order to understand the microscopic origin of the nonlinear behavior of organic NLO materials, considerable theoretical and experimental investigations have been developed by Kerkoc *et al.* (1990) and Dimitriev *et al.* (1991). The conjugated  $\pi$  electron system provides a pathway for the entire length of conjugation under the perturbation of an external electric field. Functionalization of both extremes of the  $\pi$  conjugated system with electron donor and acceptor groups could increase the asymmetric electronic distribution in the ground and excited states, thus leading to an increased optical non-linearity (Prasad *et al.* 1991). In continuation with our studies, we report herein the synthesis, characterization and NLO properties of (*E*)- and (*Z*)-3-(4-methoxyphenyl)-2-(4-nitrophenyl)-acrylic acids and the corresponding (*E*)-ethyl ester (**3**) (Scheme 1). All compounds were fully characterized by IR, UV, NMR, MS and in the case of derivatives **1** and **2** their structures were corroborated by X-ray diffraction analysis.

Compounds **1** and **2** were obtained by reaction of *p*-anisaldehyde and *p*-nitrophenylacetic in acetic anhydride and triethylamine. Both compounds were found to be poorly soluble in most organic solvents, for this reason it was difficult to study their NLO properties. In order to improve their solubility to measure NLO properties, the corresponding ethyl ester derivatives were synthesized by reaction of the acid with thionyl chloride and ethanol. It should be mentioned that when compound **1** was treated under the same reaction conditions, the product undergoes isomerization to give compound **3** (Scheme 1).



drawing application. (Farrugia *et al.* 1997) All heavier atoms were found by Fourier map difference and refined anisotropically. Some hydrogen atoms were found by Fourier map differences and refined isotropically. The remaining hydrogen atoms were geometrically modeled and are not refined.

### Syntheses

A solution of 5.44 g (0.040 mmol) of *p*-anisaldehyde and 6.69 g (0.037 mmol) of *p*-nitrophenylacetic acid in 4 ml of triethylamine and 4 ml of acetic anhydride was heated under reflux in an oil bath maintained at 150 °C for 4 h. A precipitate often forms during this heating period. The reaction mixture was acidified with 8 ml of concentrated hydrochloric acid, and the organic phase was extracted with 300 ml of methylene chloride and water. This solution was washed with several 100 ml portions of water and then extracted with three 100 ml portions of 20% sodium hydroxide. The combined extracts were then acidified to pH of 4.0 with about 15 ml of acetic acid. The *trans* acid was filtered from the solution containing the salt of the *cis* acid and washed with water. The *cis* isomer was precipitated by the addition of 15 ml of concentrated hydrochloric acid.

#### **(Z)-3-(4-methoxyphenyl)-2-(4-nitrophenyl)-acrylic acid (1) (Kertcham *et al.* 1963)**

The product was obtained as an orange solid (2.25 g 7.52 mmol), yield 20%, m.p. 234-236 °C. IR (KBr)  $\nu_{\max}$  (cm<sup>-1</sup>): 3448 (OH), 2937, 2841, 2512, 2040, 1669 (CO), 1596, 1511, 1426, 1346, 1257, 1172, 1106, 1025, 923, 854, 831, 784, 711, 654, 551; MS *m/z* (%), 300 (M<sup>+</sup>+1, 19), 299 (M<sup>+</sup>, 100), 283 (2), 269 (3), 254 (6), 208 (13), 165 (39), 137 (54), 109 (14); <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>),  $\delta$  (ppm): 3.70 (3H, s, OCH<sub>3</sub>), 6.79 (2H, d, *J*=9.0 Hz, H-3, H-5), 6.99 (2H, d, *J*=9.0 Hz, H-2, H-6), 7.47 (2H, d, *J*=8.8 Hz,

H-11, H-15), 7.81 (1H, s, H-7), 8.24 (2H, d, *J*=8.8 Hz, H-12, H-14); <sup>13</sup>C-NMR (100 MHz, DMSO-d<sub>6</sub>),  $\delta$  (ppm): 55.8 (OMe), 114.7 (C-3, C-5), 124.3 (C-12, C-14), 126.6 (C-1), 129.4 (C-8), 131.8 (C-11, C-15), 132.8 (C-2, C-6), 140.8 (C-7), 144.9 (C-10), 147.3 (C-13), 160.8 (C-4), 168.2 (C-9); Elemental analysis calcd. for C<sub>16</sub>H<sub>13</sub>NO<sub>5</sub>: C 64.21, H 4.38, N 4.68. Found: C 64.34, H 4.13, N 4.60.

#### **(E)-3-(4-methoxyphenyl)-2-(4-nitrophenyl)-acrylic acid (2) (Kertcham *et al.* 1963)**

The product was obtained as a yellow solid (0.84 g 2.80 mmol), yield 8%, m.p. 193-196 °C. IR (KBr)  $\nu_{\max}$  (cm<sup>-1</sup>): 3445 (OH), 2339, 1722 (CO), 1589, 1513, 1397, 1340, 1248, 1178, 1111, 1011, 850, 823, 753, 570; MS *m/z* (%), 300 (M<sup>+</sup>+1, 18), 299 (M<sup>+</sup>, 100), 283 (3), 269 (10), 254 (4), 208 (7), 165 (8), 137 (25), 109 (5); <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>),  $\delta$  (ppm): 3.80 (3H, s, OCH<sub>3</sub>), 7.01 (2H, d, *J*=8.8 Hz, H-3, H-5), 7.30 (1H, s, H-7), 7.53 (2H, d, *J*=8.8 Hz, H-2, H-6), 7.76 (2H, d, *J*=8.9 Hz, H-11, H-15), 8.27 (2H, d, *J*=8.9 Hz, H-12, H-14); <sup>13</sup>C-NMR (68 MHz, DMSO-d<sub>6</sub>),  $\delta$  (ppm): 55.8 (OMe), 114.7 (C-3, C-5), 124.6 (C-12, C-14), 127.2 (C-11, C-15), 127.8 (C-1), 130.9 (C-2, C-6), 131.8 (C-7), 132.8 (C-8), 143.7 (C-10), 146.9 (C-13), 160.5 (C-4), 170.8 (C-9); Elemental analysis calcd. for C<sub>16</sub>H<sub>13</sub>NO<sub>5</sub>: C 64.21, H 4.38, N 4.68. Found: C 64.34, H 4.13, N 4.60.

#### **Ethyl (E)-3-(4-methoxyphenyl)-2-(4-nitrophenyl)-acrylate (3)**

The reaction flask was first charged with a mixture of compounds **1** and **2** (450 g, 1.5mmol) in 20 ml thionyl chloride and refluxed for 2 h under N<sub>2</sub> atmosphere, excess thionyl chloride was eliminated by distillation followed by addition of 20 ml of ethanol and the solution was stirred for 24 hr. The solvent was evaporated, and ethyl acetate was added. After drying over anhydrous Na<sub>2</sub>SO<sub>4</sub> and purification by co-

lumn chromatography with a hexane:ethyl acetate mixture (9:1), the product was obtained as a yellow solid 0.45 g (91% yield) mp 77-79°C. IR (ATR)  $\nu_{\max}$  (cm<sup>-1</sup>): 2987, 2940, 1682 (CO), 1597, 1509, 1343, 1343, 1245, 1172, 1029, 853, 835 MS  $m/z$  (%), 344 (M<sup>+</sup>+1, 42), 327 (M<sup>+</sup>, 82), 282 (50), 254 (40), 254 (4), 208 (20), 165 (44), 136 (30), 73 (100); <sup>1</sup>H-NMR (400 MHz, Cl<sub>3</sub>CD),  $\delta$  (ppm): 1.29 (3H, t,  $J=7$  Hz, CH<sub>3</sub>), 3.76 (3H, s, OCH<sub>3</sub>), 4.26 (2H, q,  $J=7.0$  Hz, CH<sub>2</sub>), 6.97 (2H, d,  $J=8.9$  Hz, H-3, H-5), 7.42 (2H, d,  $J=8.8$  Hz, H-2, H-6), 7.42 (2H, d,  $J=8.9$  Hz, H-11, H-15), 7.90 (1H, s, H-7), 8.24 (2H, d,  $J=8.8$  Hz, H-12, H-14); <sup>13</sup>C-NMR (100 MHz, Cl<sub>3</sub>CD),  $\delta$  ppm: 14.2 (CH<sub>3</sub>), 55.3 (OMe), 61.3 (CH<sub>2</sub>), 114.0 (C-3, C-5), 123.8 (C-12, C-14), 126.2 (C-1), 128.2 (C-8), 131.2 (C-11, C-15), 132.4 (C-2, C-6), 141.6 (C-7), 143.7 (C-10), 147.2 (C-13), 160.7 (C-4), 166.7 (C-9);

### Third non linear optical measurements for compound **3**

The third nonlinear response susceptibility for compound **3** was measured as macroscopic nonlinear polarizability ( $\chi^{(3)}$ ) by the Maker-Fringe technique over polymeric film doped. The sample was prepared using the guest(molecule)-host(inert polymer) approach using polystyrene. Ratios of 70:30 wt % of polystyrene and chromophore **3** were dissolved in chloroform. The solid polymeric films were deposited over fused silica substrates (1 mm-thick) by using the spin coating technique. The films of **3** had a thickness of 520 nm, with a good optical quality at visible and NIR wavelength. The

thickness of the polymeric film was measured using a Dektak 6M profiler. The THG Maker-Fringes technique consists on the comparison of the oscillations in the THG intensity produced by the substrate alone and those obtained from the active film on a substrate, as a consequence of the variations in the incident angle of the pumping laser beam. Details of this experiments and THG Maker-Fringes setup can be found in the literature (Muñoz *et al.* 2008).

## RESULTS AND DISCUSSION

### Spectroscopic data

All compounds were characterized by <sup>1</sup>H and <sup>13</sup>C NMR experiments, selected data are summarized in Table 1. The singlets at 7.30, 7.81 and 7.90 ppm in the <sup>1</sup>H-NMR spectra of compounds **1**, **2** and **3** correspond to the vinylic protons.

The <sup>1</sup>H-NMR signals for the aryl rings were assigned based on their COSY spectra which allowed correlation between the protons in the ring containing the electron donor group and those of the ring with the electron acceptor group which gave two AX systems with coupling constants between 8.8 and 8.9 Hz. In the <sup>13</sup>C-NMR spectra of compounds **1**, **2** and **3**, the signals for C-4 and C-9 are shifted to high frequencies (160.5, 160.8 and 160.7 ppm for C-4 and 170.8, 168.2 and 166.7 ppm for C-9). The two isomeric acids could be identified based on the characteristic chemical shift observed for the vinylic carbon (C-7) which in (*E*)-isomer shows a marked deshielding

**Table 1.** Selected <sup>1</sup>H and <sup>13</sup>C-NMR (ppm) and Infrared (cm<sup>-1</sup>) for compounds **1-3**.

Compound	H-7	C-4	C-7	C-9	C-13	CO
<b>1</b>	7.30	160.50	131.80	170.80	146.90	1669
<b>2</b>	7.81	160.80	140.80	168.20	147.30	1722
<b>3</b>	7.90	160.73	141.57	166.73	147.23	1668

effect (140.8 ppm) compared to (*Z*)-isomer (131.8 ppm). The same trend is observed for H-7 in the proton spectra. In the IR spectra, the carbonyl band appears at 1668 and 1669  $\text{cm}^{-1}$  for the (*E*)-isomers and 1722  $\text{cm}^{-1}$  in the (*Z*)-isomer.

### Molecular structure

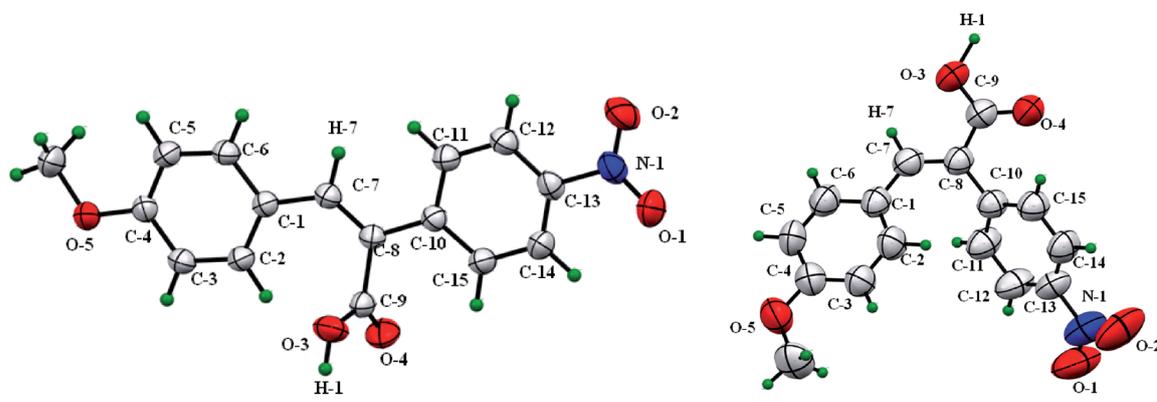
The acids **1** and **2** were crystallized by slow evaporation of a concentrated mixture of chloroform and hexane and the molecular perspectives are shown in Figure 2.

The details of the crystal data and summary of the collection parameters for acids **1** and **2** are given in Table 2. Selected bond distances and angles are compared in Table 3

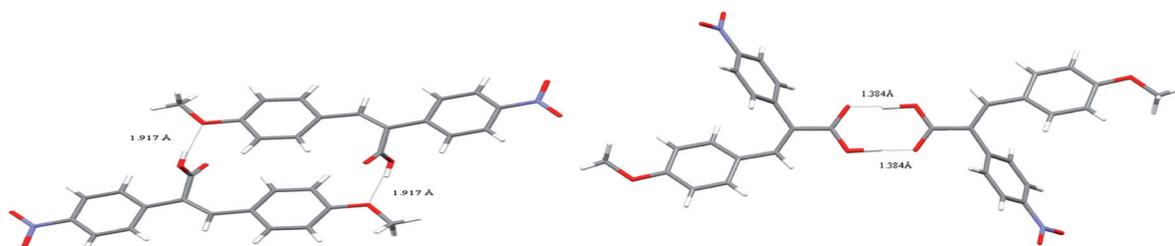
One important feature that the two

compounds share is the presence of intermolecular hydrogen bonding, in the case of compound **1** [(*Z*)-isomer], this interaction is between the carboxyl group and the methoxy group of a neighboring molecule with bond distance of 1.917 (2) Å. In contrast, in compound **2** [(*E*)-isomer] this intermolecular hydrogen bonding is between the acid groups of neighbor molecules with a bond distance of 1.384 (2) Å forming a dimeric centrosymmetric structures (Figure 3).

Several differences are identified in the relative configurations of the two compounds; Table 3 shows selected dihedral angles and torsion angles for specific fragments of each molecule. From these data it is evident that (*E*)-isomer (**2**) is considerably



**Figure 2.** Molecular perspective of compounds **1** [(*Z*)-isomer] and **2** [(*E*)-isomer].



**Figure 3.** Intermolecular hydrogen bonding in compounds **1** and **2**.

**Table 2.** Crystal data for acids **1** y **2**.

	<b>1</b>	<b>2</b>
Chemical Formula	C <sub>16</sub> H <sub>13</sub> N O <sub>5</sub>	C <sub>16</sub> H <sub>13</sub> N O <sub>5</sub>
Formula weight	299.27	299.27
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2 <sub>1</sub> /c
Unit cell dimensions		
a, [Å]	6.5697(2)	6.5267 (6)
b, [Å]	10.6569(4)	15.1735 (15)
c, [Å]	11.0720(4)	14.9585 (17)
α, [°]	101.1920(1)	90
β, [°]	104.4860(1)	95.729 (7)
γ, [°]	106.409(2)	90
Volume (Å <sup>3</sup> )	690.09(4)	1474.0 (3)
Z	2	4
Temperature	293(2)	293 (2)
Reflections collected	5064	5650
Reflections unique	3063	3089
Reflections observed (4σ)	2306	1204
Number of variables	204	252
Final R (4σ)	0.0428	0.0613
Final wR <sup>2</sup>	0.1185	0.1222
Goodness-of-fit	0.999	0.995

**Table 3.** Selected bond lengths (Å) and angles (°) for acids **1** y **2**.

Lenght (Å)	Angle (°)				
	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>	
C(7)-C(8)	1.342(2)	1.341(4)	C(10)-C(8)-C(9)-O(4)	-79.9	175.9
C(7)-C(1)	1.467(2)	1.455(4)	C(10)-C(8)-C(9)-O(3)	99.6	-2.9
C(8)-C(10)	1.481(2)	1.482(4)	C(6)-C(1)-C(7)-H(7)	-11.4	24.7
C(8)-C(9)	1.499(2)	1.458(4)	C(10)-C(8)-C(7)-H(7)	0.3	-175.9
O(5)-H(1)	1.917(2)	1.384(2)			

more sterically crowded, and as a consequence the two rings twist out of plane formed by H7-C7-C8 atoms, showing a dihedral angle of 55.7° between the planes of the two rings, as well as a torsion angle of 4.3° for the C6-C1-C7-H7 fragment.

### Lineal absorption of compound **3**

The lineal optical characterization of compound **3** was carried out in solution using solvents with different polarities. The ab-

sorption spectrum showed a broad absorption band with a maximum peak around 291 nm. A short blue shift (6 nm) is shown for the absorption band of **3** from non polar (toluene) to polar solvents (methanol). The absorption band is due to n→π\* electronic transition over the π-backbone system, which is in agreement with the *push-pull* architecture present on compound **3**. The position of the electronic transition band in the absorption spectra is affected directly for the *cis* configuration of the double bond,

reducing the conjugation process over the  $\pi$ -system (Nalwa *et al.* 1997).

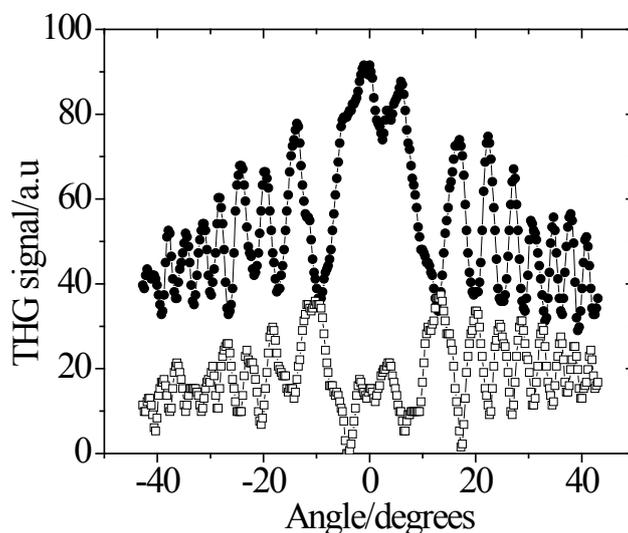
### Third non linear optical properties

The cubic non-linear (macroscopic) response of compound **3** was measured over solid film using the third harmonic generation (THG) Maker-Fringes technique at the IR wavelength (1200 nm), and the typical graph for THG responses obtained in this technique is shown in Figure 4. For derivatives **1** and **2** their insolubility properties in common organic solvents precluded optical characterization in solid film. The macroscopic nonlinear susceptibility  $\chi^{(3)}$  was used to calculate the second hyperpolarizability  $\gamma$ , which is the molecular parameter of interest, through  $\gamma = \chi^{(3)}/L^4 N_s$  where  $N_s$  is the density of molecules in the polymer film.  $L = (n^2 + 2)/3$  is the correction factor due to local field effects and  $n$  is the refractive index. Assuming for the film the refractive index and density of polystyrene, and using a molecular doping level of 30%, the  $\gamma$  value for compound **3** resulted to be  $763 \times 10^{-36}$  esu, which is in the is longer than the values calculated for

other derivatives of stilbene ( $63\text{--}228 \times 10^{-36}$  esu) (Romaniello *et al.* 2004). It has been reported that the non linear responses of organic molecules are related to the polarization of the  $\pi$ -electronic system which is dependent on structural parameters such as the length of the  $\pi$ -backbone and configuration (Bredes *et al.* 1994). The non linear response measured for derivative **3** is affected directly by the *E* configuration of the stilbene, which could be responsible for the low value.

### CONCLUSIONS

The isomeric *push-pull* acids (*Z*-**1** and *E*-**2**) were prepared and characterized. Attempts to prepare the ethyl ester derivatives in order to increase their solubility and to study their. NLO properties lead to isomerization of (*Z*-**1** to the (*E*)-isomer (compound **3**). The non linear response measured for derivative **3** is affected by the *Z* configuration of the aromatic rings in the stilbene, which could be responsible for the low value observed. However, experimental second hyperpola-



**Figure 4.** Third-harmonic light pattern as a function of the incident angle for a thin polymer film (520 nm) (filled circles) doped with 30 wt.% of compound **3**, and for the 1 mm thick fused silica substrate alone (open circles). The fundamental wavelength is 1200 nm.

riability obtained for compound **3** is longer than those values theoretically estimated for other stilbene derivatives.

CCDC-905466 and CCDC-905467 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html), or from the Cambridge Crystallographic Data Centre 12, Union Road, Cambridge CB2 1EZ, UK;

fax: (+44) 1223 336033; or e.mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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