# Comparison of Alkoxy-substituted 4,4′-Distyrylbiphenyls and the Corresponding 4,4′-Distyrylbenzenes

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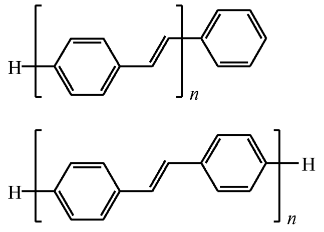
Configurationally highly pure (*E,E*)-4,4′-bis(styryl)biphenyls **2a** – **e** were obtained by Siegrist reactions of 4,4′-dimethylbiphenyl **3** and alkoxy-substituted benzaldimines (**4a** – **e**). DSC measurements have indicated different crystalline modifications of these conjugated compounds. The stilbenoid chromophores of **2a** – **e** are compared to the stilbenoid chromophores in the OPV series, which have a similar length of conjugation. The intense fluorescence and the high transparency in the visible region are promising properties for an application of the donor-substituted compounds **2a** – **e** in two-photon absorption (TPA) techniques.

*Key words:* Absorption, Condensation Reaction, Conjugation, Fluorescence

## Introduction

Monomeric, oligomeric and polymeric stilbenoid systems represent an attractive class of compounds in materials science, because their tunable chromophores, fluorophores and electrophores find numerous applications as optical brighteners, laser dyes, scintillators, optical switches, nonlinear optical systems (NLO), imaging systems, semiconductors, photoconductors, electroluminescent devices (LED), field effect transistors (FET), *etc.* [1].

Whereas more than 1000 publications and patents exist on substituted oligo- and polyphenylenevinylenes (OPV, PPV) **1**, very little is known about conjugated systems **2** of (*E*)-stilbene building blocks, which are arranged in a way that biphenyl units are segments of the chain (Fig. 1).



**1**

**2**

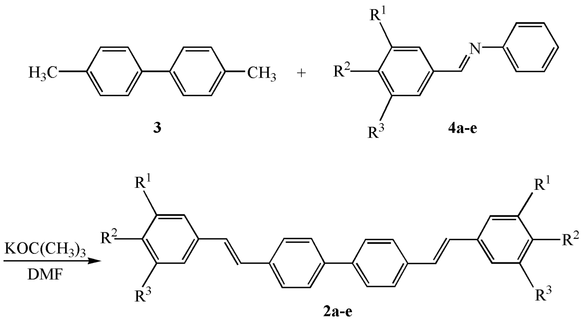
Fig. 1. Arrangement of (*E*)-stilbene building blocks in conjugated chains.

The conjugation length of members of the series **1** and **2** increases with increasing numbers *n* of repeat units, but it is confined by the so-called effective conjugation length $n_{\mathrm{ECL}}$ [2, 3]. According to the perturbation theory, even oligomers, which would have a completely planar geometry, have such a confinement, because of the different bond lengths (different resonance integrals) in the chain [1k, 4]. However, the convergence of the absorption or fluorescence maxima for $n \rightarrow n_{\mathrm{ECL}}$ is accelerated, that means $n_{\mathrm{ECL}}$ is decreased, when torsions appear along the chain. The biphenyl building blocks, present in **2**, are much more twisted than the styryl units present in **1**. Therefore it is interesting to compare systems **1** and **2** of similar chain length.

We started to prepare compounds **2** which bear long alkoxy chains on the terminal benzene rings. These groups enhance the solubility, and their donor character generates quadrupolar molecules with a high two-photon absorption cross-section. Two-photon absorption (TPA) has a lot of important applications in laser scanning fluorescence imaging [5], microfabrication [6], three-dimensional data storage [7], photodynamic therapy [8], *etc.*

## Results and Discussion

Among the methods for the formation of olefinic double bonds, the kinetically controlled Siegrist reaction [9, 10] has the advantage of an extremely high *trans* selectivity. The obtained *trans/cis* ra-



| 2 | a | b | c | d | e |
|---|---|---|---|---|---|
| $R^1$ | $OC_{12}H_{25}$ | $OC_{12}H_{25}$ | $OCH_3$ | $OC_6H_{13}$ | $OC_{12}H_{25}$ |
| $R^2$ | H | $OC_{12}H_{25}$ | $OC_{12}H_{25}$ | $OC_6H_{13}$ | $OC_{12}H_{25}$ |
| $R^3$ | H | H | $OCH_3$ | $OC_6H_{13}$ | $OC_{12}H_{25}$ |
| Yield (%) | 61 | 80 | 57 | 70 | 44 |
| M. p. (°C) | 328 (dec.) | 176 | 137 | 80 | 90 |

Scheme 1. Preparation of the target compounds **2a**–**e**.

tio is above the thermodynamic equilibrium, which in the stilbenoid series is usually in the range of 95 : 5. Thus, highly pure (*E*,*E*) configurations of the 4,4′-bis(styryl)biphenyls **2a**–**e** could be prepared (Scheme 1) in good yields. 4,4′-Dimethyldiphenyl (*p*-ditolyl) **3** was condensed with the aldimines **4a**–**e** in a strongly alkaline medium. The strict *anti* elimination of aniline effects the high stereoselectivity.

The (*E*,*E*) configurations of **2a**–**e** are documented by the AB spin patterns of the olefinic protons with coupling constants of 16.5 ± 0.2 Hz. The inner olefinic protons are shifted to higher field ($\delta = 6.96 \pm 0.05$) compared to the outer olefinic protons ($\delta = 7.06 \pm 0.04$). The $^{13}C$ chemical shifts of the olefinic carbon atoms indicate a corresponding effect ($1.6 \le \Delta\delta \le 1.8$ ppm) [11]. Moreover, $^1H$ NMR measurements revealed the absence of (*E*,*Z*) and (*Z*,*Z*) configurations. (The detection limit amounts to 1 %).

The compounds **2a**–**e** are solid yellow materials, which can exist in different crystalline modifications. Fig. 2 shows the differential scanning calorimetry (DSC) of **2e**. The cooling process (upper curve) contains three exothermic phase transitions (onset temperature in °C; negative $\Delta H$ values in kJ mol$^{-1}$):

$$\mathrm{I} \xrightarrow[-21]{77} \mathrm{Cr}_1 \xrightarrow[-8]{66} \mathrm{Cr}_2 \xrightarrow[-1]{99} \mathrm{Cr}_3$$

In the heating process (lower curve), the peak of the two higher phase transitions of **2e** are split into two peaks, each. The onset temperatures of the heating curve peaks are: 43, 69, 70, 84, and 89 °C. Although structure **2e** appears as a phasmidic system, liquid crystals are not formed. The other compounds **2a**–**d** behave similarly – with two exceptions: **2a** has only one crystalline phase between r. t. and 32.8 °C, and **2d** exhibits an additional exothermic transition in the heating curve (Fig. 3). Repeating of the DSC measurements did not change the effects observed previously in the heating and cooling curves.

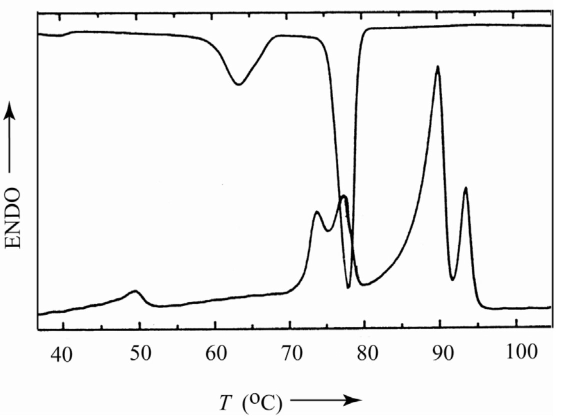


Fig. 2. DSC heating and cooling curve of **2e**. Measurement with a rate of 10 K min$^{-1}$.

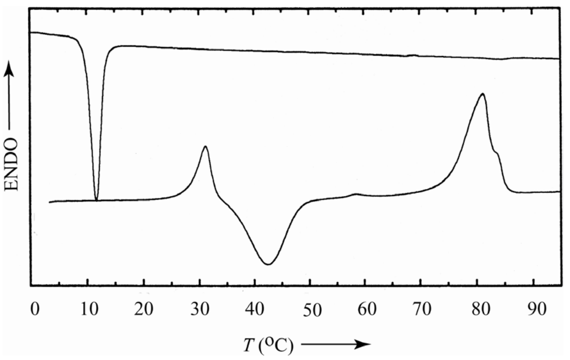


Fig. 3. DSC heating and cooling curve of **2d**. Measurement with a rate of 10 K min$^{-1}$.

The most important properties of the newly synthesized 4,4′-bis(styryl)biphenyls **2** concern their absorption and fluorescence. The long-wavelength absorption band (for **2** in $CH_2Cl_2$) has a maximum at 365 ± 5 nm. A band with a maximum at 449 ± 3 nm is observed for the intense fluorescence. The Stokes shift amounts to about 5200 cm$^{-1}$. Table 1 shows a comparison of the data for **2e** with those of related OPVs **5** [12, 13] and **6** [14, 15].

Although the length *l* of the stilbenoid chromophores [11] increases from **5** *via* **2e** to **6**, the $\lambda_{max}$ values of absorption and fluorescence of **2e** are

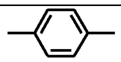
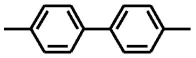
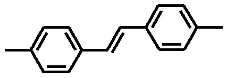
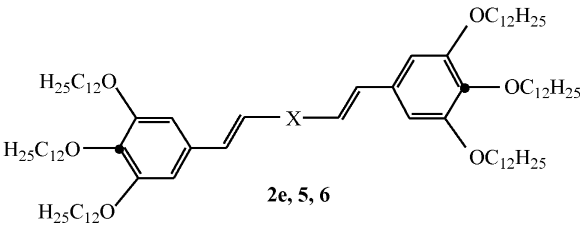
| Compd. | Core —X— | Length •—• $l$ (nm) | Absorption $\lambda_{max}$ (nm) | Fluorescence $\lambda_{max}$ (nm) |
|---|---|---|---|---|
| **5** |  | 1.60 | 374 | 450/442 |
| **2e** |  | 1.88 | 365 | 447 |
| **6** |  | 2.26 | 399 | 469 |

Table 1. Comparison of the absorption and fluorescence of the conjugated systems **5**, **2e** and **6** ($CH_2Cl_2$, fluorescence excitation at 366 nm).



**2e, 5, 6**

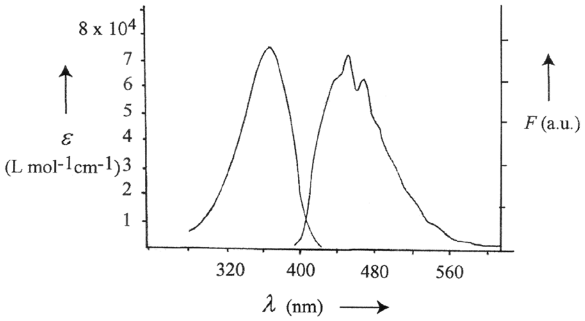


Fig. 4. Absorption [$\varepsilon = f(\lambda)$] and fluorescence $F = f(\lambda)$ of **2e** in $CH_2Cl_2$; excitation wavelength of the fluorescence: 366 nm.

the lowest in this series. As assumed in the introduction, the higher torsion angle between the neighboring benzene rings in **2e** impairs the conjugation. Fig. 4 shows absorption and fluorescence spectra of **2e**. In contrast to the absorption band, the fluorescence band of **2e** exhibits a vibration finestructure, which suggests that the excited molecules are more planar. The tailing of the fluorescence band (520 – 620 nm) is probably due to aggregates of the J type.

We selected **2e** for the measurement of the fluorescence quantum yield and found the high value of 79 %, which corresponds to the dimer and trimer in the OPV series [11].

## Conclusions

The Siegrist reaction yielded 4,4′-bis(styryl)biphenyls (**2a** – **e**) in highly pure (*E*,*E*) configurations. Alkoxy groups on the terminal benzene rings enhance the solubility and effect as electron donor groups an intramolecular charge transfer. The long-wavelength band of **2** is – compared to other conjugated stilbenoid compounds – somewhat blue-shifted, so that the transparency in the visible region is very good. Together with the high fluorescence intensity and the quadrupolar character of **2**, this behavior makes the compounds excellent candidates for two-photon absorption techniques.

## Experimental Section

Melting points were obtained on a Büchi melting point apparatus and are uncorrected. The DSC measurements were performed on a Perkin-Elmer instrument DSC 7. A Zeiss MCS 224/MCS 234 diode array spectrometer served for the UV/Vis and a Perkin-Elmer LS 50B spectrometer for the fluorescence measurements. The $^1H$ and $^{13}C$ NMR spectra were obtained on Bruker AM 400 and AC 200 instruments. For FD MS measurements a Finnigan MAT 95 spectrometer was used. The IR spectra were measured with a Beckman Acculab. Elemental analyses were obtained in the microanalytical department of the Institute of Organic Chemistry of the University of Mainz.

The measurement of the fluorescence quantum yield of **2e** in $CH_2Cl_2$ was performed according to the described method [14]. (*E*,*E*)-1,4-Bis(styryl)benzene served as standard with $\phi_F = 0.90$ [16].

### *General procedure for the preparation of the (E,E)-4,4′-bis(2-phenylvinyl)biphenyls **2a** – **e***

A stream of dry, oxygen-free nitrogen was purged for 30 min through a solution of 4,4′-dimethylbiphenyl (**3**) [17] (0.55 g, 3.0 mmol) in 150 mL of DMF. Then $KOC(CH_3)_3$ (1.35 g, 12.0 mmol) was added to the solution and after further 10 min stirring 3.0 mmol of the benzaldimine **4a** [18, 19], **4b** [13], **4c** [20], **4d** [14], or **4e** [13]. After 1 h at 90 °C the reaction was stopped by dropwise addition of 150 mL of $H_2O$ and 100 mL of 10 % HCl. The formed precipitate was carefully washed with $H_2O$ and $CH_3OH$. The less soluble products were directly recrystallized: **2a** from *o*-dichlorobenzene, **2b** from chloroform, and

**2c** from toluene/isopropanol (1 : 2). The more soluble products **2d** and **2e** were filtered over $SiO_2$ (10 × 15 cm, $CH_2Cl_2$) and then recrystallized from isopropanol.

### *(E,E)-4,4′-Bis[2-(4-dodecyloxyphenyl)vinyl]biphenyl (**2a**)*

Yellow crystals, yield 1.32 g (61 %), m. p. 328 °C (decomp.). – IR (KBr): $\nu$ = 2900, 2830, 1590, 1495, 1270, 1165, 960, 825 cm$^{-1}$. – $^{1}$H NMR ($C_2D_2Cl_4$, $T$ = 373 K): $\delta$ = 0.88 (t, 6H, $CH_3$), 1.25 (m, 32H, $CH_2$), 1.45 (m, 4H, $CH_2$), 1.75 (m, 4H, $CH_2$), 3.96 (t, 4H, $OCH_2$), 6.88/7.40 (AA′BB′, 8H, arom. H, outer benzene rings), 6.95/7.05 (AB, $^{3}J$ = 16.4 Hz, olefin. H), 7.50/7.58 (AA′BB′, 8H, aromat. H, inner benzene rings) [21]. – FD MS: *m/z* ( %) = 726 (100) [M]$^{+}$. – $C_{52}H_{70}O_2$ (727.3): calcd. C 85.90, H 9.70; found C 85.73, H 9.51.

### *(E,E)-4,4′-Bis[2-(3,4-didodecyloxyphenyl)vinyl]biphenyl (**2b**)*

Yellow crystals, yield 2.64 g (80 %), m. p. 176 °C. – IR (KBr): $\nu$ = 2895, 2830, 1505, 1455, 1260, 1240, 1220, 1125, 960, 805 cm$^{-1}$. – $^{1}$H NMR ($CDCl_3$, $T$ = 323 K): $\delta$ = 0.89 (t, 12H, $CH_3$), 1.24 (m, 64H, $CH_2$), 1.45 (m, 8H, $CH_2$), 1.80 (m, 8H, $CH_2$), 4.03 (t, 8H, $OCH_2$), 4.08 (t, 8H, $OCH_2$), 6.87/7.03/7.08 (ABC, 6H, aromat. H, outer benzene rings), 6.97/7.06 (AB, $^{3}J$ = 16.5 Hz, olefin. H), 7.53/7.59 (AA′BB′, 8H, aromat. H, inner benzene rings) [21]. – FD MS: *m/z* ( %) = 1095 (100) [M]$^{+}$. – $C_{76}H_{118}O_4$ (1095.8): calcd. C 83.31, H 10.85; found C 83.09, H 10.55.

### *(E,E)-4,4′-Bis[2-(4-dodecyloxy-3,5-dimethoxyphenyl)vinyl]-biphenyl (**2c**)*

Pale yellow crystals, yield 1.44 g (57 %), m. p. 137 °C. – IR (KBr): $\nu$ = 2900, 2835, 1570, 1495, 1455, 1410, 1235, 1120, 960, 820 cm$^{-1}$. – $^{1}$H NMR ($CDCl_3$): $\delta$ = 0.87 (t, 6H, $CH_3$), 1.24 (m, 32H, $CH_2$), 1.45 (m, 4H, $CH_2$), 1.75 (m, 4H, $CH_2$), 3.90 (s, 12H, $OCH_3$), 3.98 (t, 4H, $OCH_2$), 6.74 (s, 4H, aromat. H, outer benzene rings), 7.02/7.08 (AB, $^{3}J$ = 16.5 Hz, 4H, olefin. H), 7.56/7.61 (AA′BB′, 8H, aromat. H, inner benzene rings). – $^{13}$C NMR ($CDCl_3$): $\delta$ = 14.1 ($CH_3$), 22.7, 25.9, 29.3, 29.5, 29.6, 29.7, 30.1, 31.9 ($CH_2$, partly superimposed), 56.3 ($OCH_3$), 73.7 ($OCH_2$), 104.0 (aromat. CH, outer benzene rings), 126.9, 127.1 (aromat. CH, inner benzene rings), 127.4, 129.0 (olefin. CH), 132.8, 136.5, 137.7, 139.6, 153.7 (aromat. $C_q$). – FD MS: *m/z* ( %) = 847 (100) [M]$^{+}$. – $C_{56}H_{78}O_6$ (847.2): calcd. C 79.39, H 9.28; found C 79.14, H 9.14.

### *(E,E)-4,4′-Bis[2-(3,4,5-trihexyloxyphenyl)vinyl]biphenyl (**2d**)*

Yellow crystals, yield 2.01 g (70 %), m. p. 80 °C. – IR (KBr): $\nu$ = 2920, 2845, 1570, 1495, 1425, 1125, 960 cm$^{-1}$. – $^{1}$H NMR ($CDCl_3$): $\delta$ = 0.88 (t, 18H, $CH_3$), 1.30 (m, 24H, 1.49 (m, 12H, $CH_2$), 1.48 (m, 12H, $CH_2$), 1.81 (m, 12H, $CH_2$), 3.97 (t, 4H, $OCH_2$), 4.02 (t, H, $OCH_2$), 6.75 (s, 4H, aromat. H, outer benzene rings), 7.00/7.09 (AB, $^{3}J$ = 16.5 Hz, 4H, olefin. H), 7.65/7.69, (AA′BB′, 8H, aromat. H, inner benzene rings). – $^{13}$C NMR ($CDCl_3$): $\delta$ = 14.0, 14.1 ($CH_3$), 22.6, 22.7, 25.8, 29.4, 30.3, 31.6, 31.8 ($CH_2$), 69.3, 73.6 ($OCH_2$), 105.4 (aromat. CH, outer benzene rings), 126.8, 127.0 (aromat. CH, inner benzene rings), 127.2, 129.0 (olefin. CH), 132.5, 136.6, 138.5, 139.6, 153.4 (aromat. $C_q$). – FD MS: *m/z* ( %) = 959 (100) [M]$^{+}$. – $C_{64}H_{94}O_6$ (959.5): calcd. C 80.12, H 9.88; found C 79.92, H 9.80.

### *(E,E)-4,4′-Bis[2-(3,4,5-tridodecyloxyphenyl)vinyl]biphenyl (**2e**)*

Yellow crystals, yield 1.93 g (44 %), m. p. 90 °C. – IR (KBr): $\nu$ = 2890, 2820, 1560, 1485, 1450, 1415, 1315, 1105, 950, 815 cm$^{-1}$. – $^{1}$H NMR ($CDCl_3$): $\delta$ = 0.88 (t, 18H, $CH_3$), 1.29 (m, 96H, $CH_2$), 1.48 (m, 12H, $CH_2$), 1.83 (m, 12H, $CH_2$), 4.01 (t, 4H, $OCH_2$), 4.05 (t, 8H, $OCH_2$), 6.75 (s, 4H, aromat. H, outer benzene rings), 7.00/7.09 (AB, $^{3}J$ = 16.5 Hz, 4H, olefin. H), 7.58/7.64 (AA′BB′, 8H, aromat. H, inner benzene rings). – $^{13}$C NMR ($CDCl_3$): $\delta$ = 14.1 ($CH_3$), 22.7, 26.1, 29.4, 29.4, 29.7, 29.7, 31.9 ($CH_2$, partly superimposed), 69.1, 73.5 ($OCH_2$), 105.2 (aromat. CH, outer benzene rings), 126.8, 127.0 (aromat. CH, inner benzene rings), 127.1, 129.0 (olefin. CH), 132.5, 136.5, 138.3, 139.5, 153.3 (aromat. $C_q$). – FD MS: *m/z* ( %) = 1465 (100) [M]$^{+}$. – $C_{100}H_{166}O_6$ (1464.4): calcd. C 82.02, H 11.43; found C 82.04, H 11.48.

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