


Proceeding Paper

# Synthesis of 4'-Alkoxy-4-( $\omega$ -cinnamoylalkoxy)azobenzenes and Their Photoswitchable Behavior <sup>†</sup>

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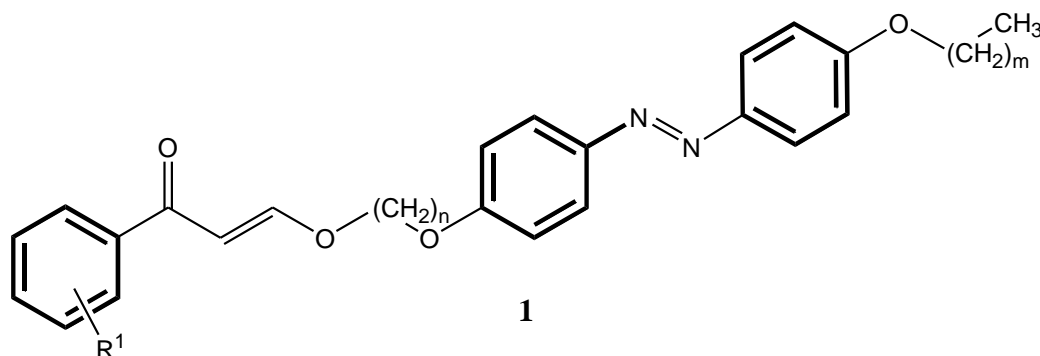
<sup>†</sup> Presented at the 25th International Electronic Conference on Synthetic Organic Chemistry, 15–30 November 2021; Available online: <https://ecsoc-25.sciforum.net/>.

**Abstract:** In search of new thermotropic, photoswitchable materials, a number of 4'-alkoxy-4-( $\omega$ -cinnamoylalkoxy)azobenzenes were prepared. The synthetic procedure included O-alkylation of 4-nitrophenol, followed by reduction of the nitro group (H<sub>2</sub>, Pd/C), diazotization of the aniline, and subsequent reaction with  $\omega$ -hydroxyalkoxybenzenes, followed by a modified Appel-type esterification (BrCCl<sub>3</sub>, PPh<sub>3</sub>). The photochemical behavior of the substances was investigated.

**Keywords:** photoswitchable materials; 4'-alkoxy-4-( $\omega$ -cinnamoylalkoxy)azobenzene; modified Appel-type esterification

## 1. Introduction

Photoswitchable molecules are able to isomerize between at least two metastable forms when photoirradiated [1]. These types of molecules have found interest in different areas in physics, chemistry, and biology [2–5]. Photoswitchable molecules have a wide range of applications, which include their use in photoelectric cells. They are also utilized in the generation of three-dimensional animations and images, as well as in screen displays in conjunction with liquid crystals [6]. Photoswitching molecules can be used as dopants in liquid crystalline hosts. Alternatively, photoswitching compounds can be liquid crystalline themselves, where often the photoswitching unit is an azobenzene. Thus, azobenzene derivatives have been utilized in photoresponsive functional devices in smart polymers [7], in molecular switches [8], in data storage systems [9], and as molecular “machines” in supramolecular organic chemistry [10–12]. In this regard, 4'-alkoxy-4-( $\omega$ -cinnamoylalkoxy)azobenzenes of type **1** (Figure 1) were prepared as potentially photoswitchable compounds with the azo- and cinnamoyl functions as two photoreactive groups [13].



**Figure 1.** 4'-alkoxy-4-( $\omega$ -cinnamoylalkoxy)azobenzene (**1**).



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## 2. Experimental Part

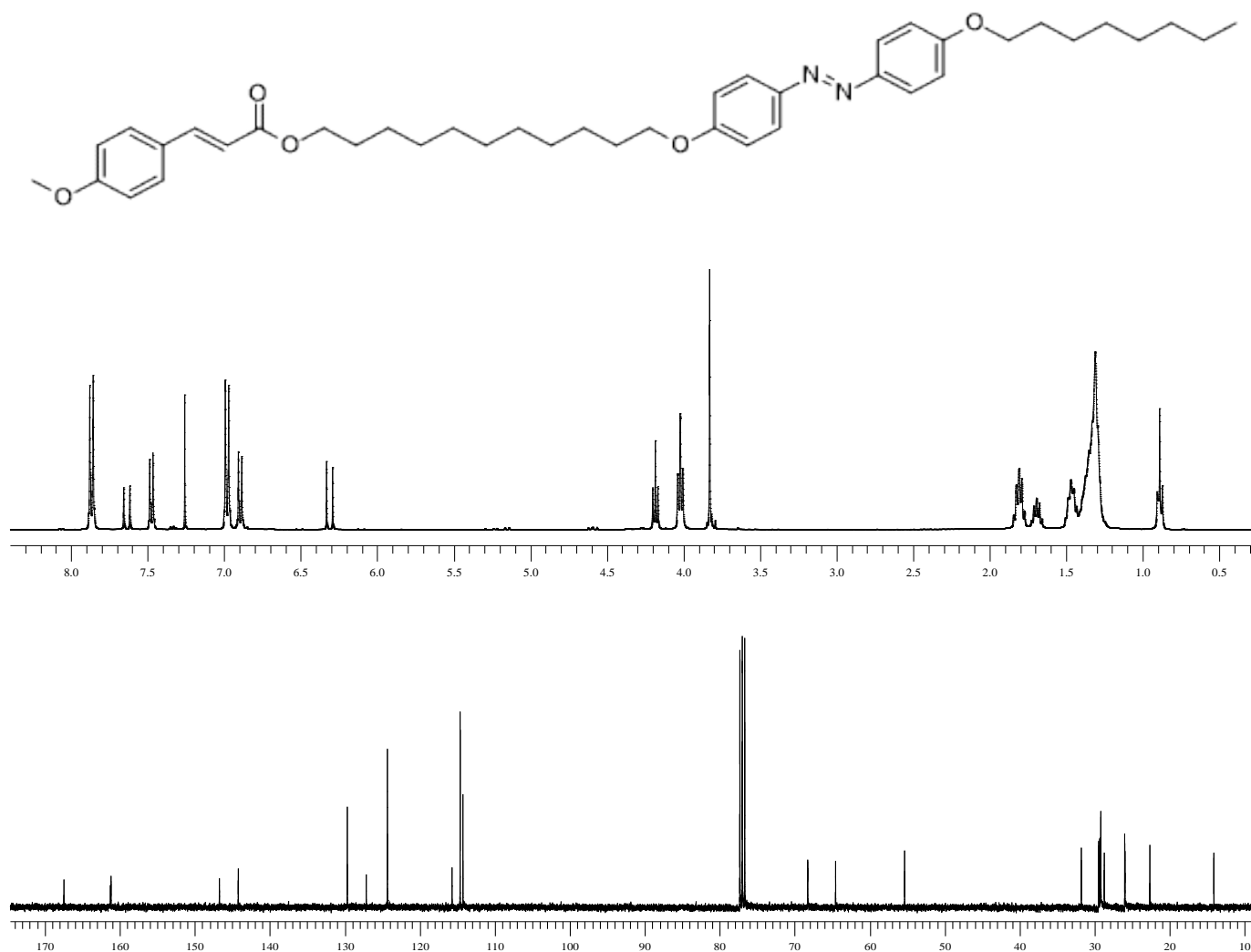
**General.** The compounds were synthesized, purified (using crystallization or column chromatography), and characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, DEPT, and/or INEPT techniques, LC-MS-MS, and IR spectroscopy. Selected compounds were analyzed by UV-Vis spectroscopy and submitted to DSC thermal analysis and X-ray single-crystal structural determination. Selected azo-cinnamates were photoirradiated in an attempt to photoisomerize the molecules. The progress of the photoreactions was followed by either UV-Vis or  $^1\text{H}$  NMR spectroscopy.

Column chromatography was carried out on commercial 60 Å silica gel (230–400 mesh, Merck grade 9385, Sigma-Aldrich) and on recycled silica gel. Analytical thin-layer chromatography (TLC) was carried out on TLC-Alu-foils from Fluka (with a fluorescent indicator at  $\lambda = 254$  nm).  $^1\text{H}$  NMR (at 400 MHz) and  $^{13}\text{C}$  NMR (at 100.5 MHz) spectra were taken on a Varian 400 MHz spectrometer. Infrared spectra were taken on a Thermo Nicolet Nexus 670 FT-IR spectrometer (solid samples as KBr pellets). UV-Vis spectroscopy was performed on a UV-1800 (Shimadzu) spectrophotometer. For photoirradiation experiments, a Luzchem LZC 4V photoreactor was used with either 13 USHIO G8T5 lamps (7.2 W low-pressure mercury arc lamps with a radiation peak at  $\lambda = 253.7$  nm) or with 14 Hitachi FL8BL-B (0.75 W, UV irradiance  $8.0$  ( $\mu/\text{cm}^2$ ), with a radiation peak at  $\lambda = 352$  nm).  $\text{CH}_2\text{Cl}_2$  (Sigma-Aldrich, purris. pa,  $\geq 99.9\%$  (GC)) and benzene were used as solvents in the photoirradiation experiments. Mass spectrometry on the synthesized compounds was performed using a LC-MS-MS 8060 (Shimadzu) with Dr. Iltaf Khan.

### *Synthesis of (E)-11-(4-((E)-4-(Octyloxy)phenyl)diazenyl)phenoxy)undecyl 3-(4-methoxyphenyl)acrylate (1a) by Modified Appel Reaction:*

To a solution of triphenylphosphine ( $\text{PPh}_3$ , 970 mg, 3.70 mmol) in dry  $\text{CH}_2\text{Cl}_2$ , (15 mL) bromotrichloromethane ( $\text{BrCCl}_3$ , 720 mg, 3.63 mmol) was added dropwise, and the resulting solution was stirred at reflux temperature for 25 min, during which it turned yellow-brown. Thereafter, 3-(4-methoxyphenyl)acrylic acid (**9a**, 530 mg, 3.00 mmol) was added, and the mixture was stirred at reflux temperature for 30 min. Then, **8a** (600 mg, 1.21 mmol) was added, and the mixture was stirred at reflux temperature for an additional 14 h. The cooled solution was submitted directly to column chromatography on silica gel ( $\text{CH}_2\text{Cl}_2$ ) to give **1a** (625 mg, 78.5%) as a yellow solid (Figure 2).

$\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ): 0.88 (3H, t,  $\text{CH}_3$ ,  $^3J = 6.8$  Hz), 1.24–1.84 (24H, m,  $\text{CH}_2$ ), 3.83 (3H, s,  $\text{OCH}_3$ ), 4.02 (4H, t,  $\text{OCH}_2$ ,  $^3J = 6.7$  Hz), 4.18 (2H, t,  $\text{OCH}_2$ ,  $^3J = 6.5$  Hz), 6.31 (1H, d, CH,  $^3J = 16.0$  Hz), 6.89 (2H, d, CH,  $^3J = 8.0$  Hz), 6.98 (4H, d, CH,  $^3J = 8.0$  Hz), 7.47 (2H, d, CH,  $^3J = 8.0$  Hz), 7.63 (1H, d, CH,  $^3J = 16.0$  Hz), 7.86 (4H, d, CH,  $^3J = 8.0$  Hz);  $\delta_{\text{C}}$  (100.5 MHz,  $\text{CDCl}_3$ ): 14.1 ( $\text{CH}_3$ ), 22.6 ( $\text{CH}_2$ ), 25.9 ( $\text{CH}_2$ ), 26.0 ( $\text{CH}_2$ ), 28.7 ( $\text{CH}_2$ ), 29.2 ( $\text{CH}_2$ ), 29.2 ( $\text{CH}_2$ ), 29.2 ( $\text{CH}_2$ ), 29.3 ( $\text{CH}_2$ ), 29.3 ( $\text{CH}_2$ ), 29.4 ( $\text{CH}_2$ ), 29.5 ( $\text{CH}_2$ ), 31.8 ( $\text{CH}_2$ ), 55.3 ( $\text{OCH}_2$ ), 68.2 ( $\text{OCH}_2$ ), 68.2 ( $\text{OCH}_2$ ), 68.3 ( $\text{OCH}_2$ ), 114.2 (CH), 114.6 (CH), 115.7 (CH), 124.3 (CH), 127.1 (CH), 129.6 (CH), 144.2 (CH), 146.7 (CH), 161.1 (CH), 161.2 (CH), 167.4 (C=O);  $\nu$  IR (KBr,  $\text{cm}^{-1}$ ): 3429, 2029, 2851, 1702, 1632, 1602, 1580, 1514, 1496, 1473, 1289, 1243, 117, 1027, 842. **Mass found:** 657.



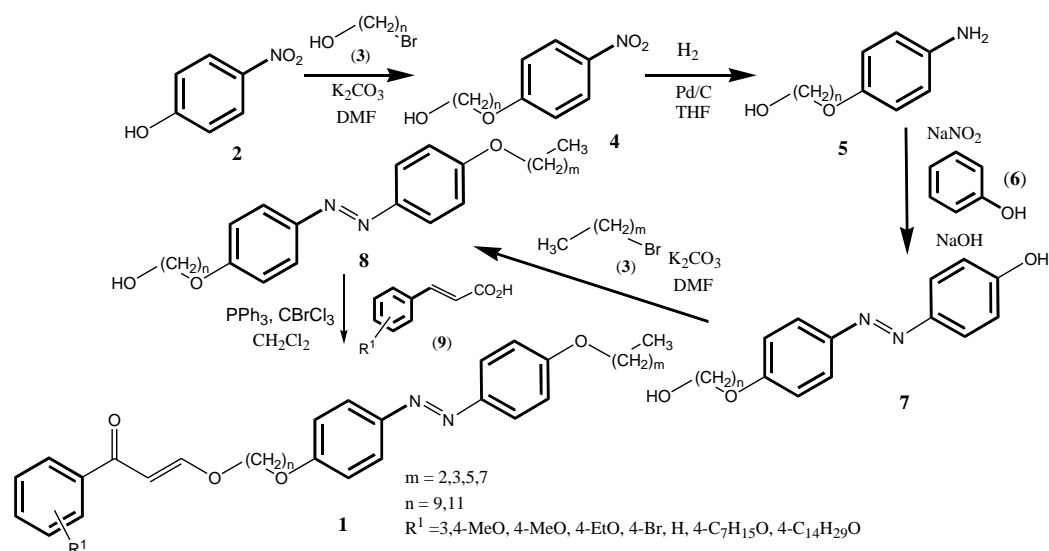
**Figure 2.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectral data of (E)-11-(4-((E)-4-(octyloxy)phenyl)diazenyl)phenoxyundecyl 3-(4-methoxyphenyl)acrylate (**1a**).

### 3. Results and Discussion

#### 3.1. Synthesis of the Target Compounds

The syntheses of target compound **1** started with commercially available 4-nitrophenol (**2**), which was subjected to a Williamson ether synthesis with various, commercially available  $\omega$ -bromoalkan-1-ols (**3**). With the relatively acidic phenol system,  $K_2CO_3$  can be used as a base. Some of the products **4** were gained by simple extraction; some of the products needed to be purified by column chromatography on silica gel. Next, the nitro group in **4** needed to be reduced. There are various ways to reduce nitrobenzenes to anilines, such as with low valent metals, zinc, and tin, in an acidic medium [14]. Also, a reduction with samarium is possible [15]. Efficient, however, is the hydrogenation of nitrobenzenes over metal catalysts as little solid waste is created as a side product. Typical metal catalysts for this reaction are Raney Nickel [16], finely divided nickel on solid [17], also in the form of Urushibara nickel, as well as platinum oxide  $PtO_2$ . Also, palladium on carbon can be used as hydrogenation catalyst. The hydrogenation of compounds **4** over 10w% Pd/C in THF using externally supplied hydrogen was successful, and anilines **5** were produced almost quantitatively. No extensive purification of the products was necessary. Because of safety concerns, later  $NaBH_4$ -acetic acid was used as an internal hydrogen source [18]. These reactions, however, were very slow to complete at the reaction scale used. Next, the obtained anilines **5** were subjected to a diazotization ( $NaNO_2$ , HCl) in the presence of phenol (**6**) to give diazobenzenes **7**. The reaction was not easy to perform,

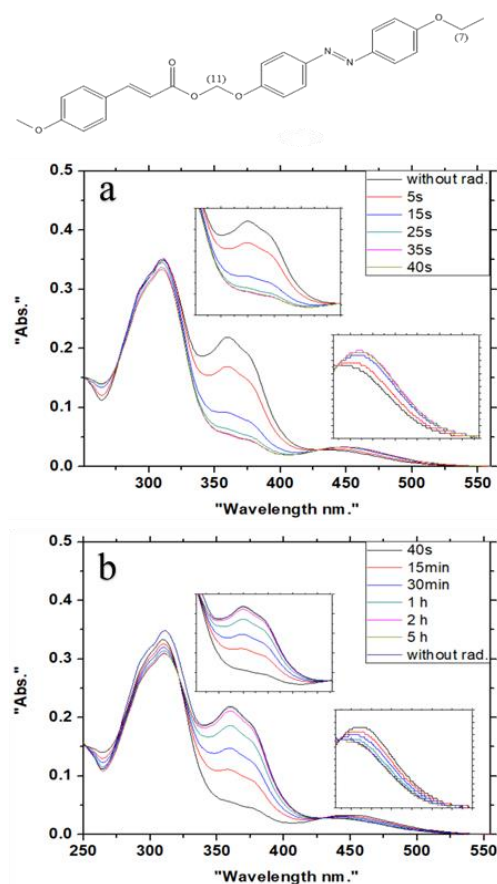
and reaction yields varied. The diazobenzenes **7** were alkylated at the phenol OH using  $K_2CO_3$  as base. The base was not strong enough to also deprotonate the alcohol function in **7**, so that the alkylation proceeded at the phenolic OH only, giving products **8**, although the reaction temperature needed was quite high ( $120\text{ }^\circ\text{C}$ ). For the preparation of azo-cinnamates **1**, the final step was an esterification reaction. For this, we decided to generate cinnamoyl halides in situ, via an Appel reaction, utilizing the system  $BrCCl_3$ ,  $PPh_3$ ,  $Et_3N$  [19], which were then reacted with **8** (Scheme 1).



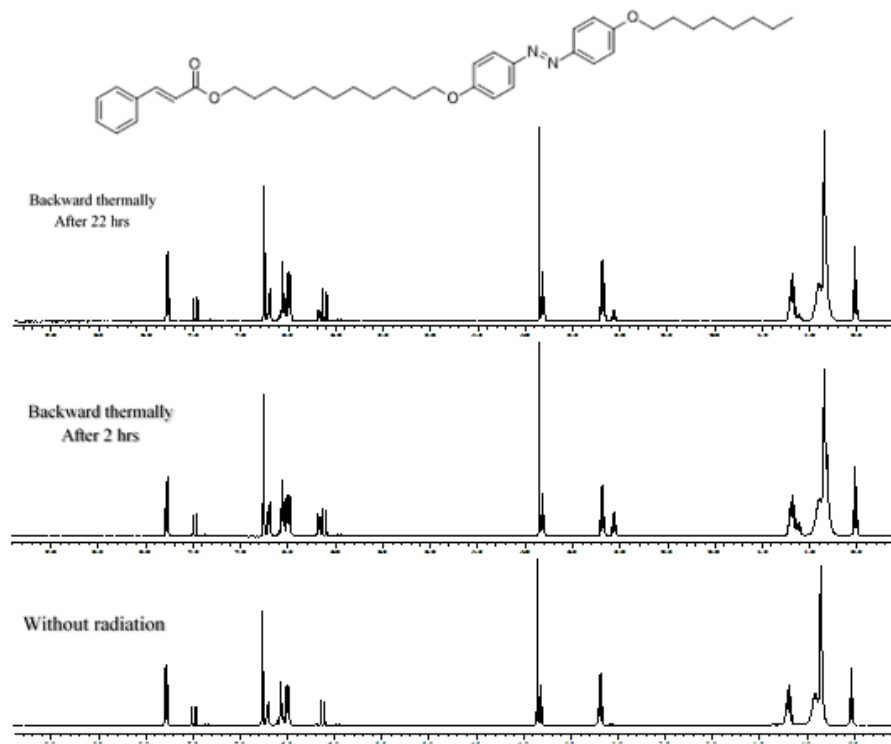
**Scheme 1.** Synthesis of the Target Compounds.

### 3.2. Photoirradiation of the 4'-Alkoxy-4-( $\omega$ -cinnamoylalkoxy)azobenzenes

On the UV spectrum, the 4'-alkoxy-4-( $\omega$ -cinnamoylalkoxy)azobenzenes **1**, prepared above, show well-separated absorption maxima, with the absorption of the azobenzene unit at  $\lambda = 360\text{ nm}$ , and a variable absorption of cinnamate moiety of  $\lambda = 259\text{--}325\text{ nm}$ , depending on the substitution pattern of the cinnamate (Figure 3). The main idea was to trigger only the azo group in the synthesized azo-cinnamates **1**, while leaving the *trans*-double bond of the cinnamate unit untouched by irradiating the molecules at  $\lambda = 350\text{ nm}$ , close to the absorption maximum of the azobenzene moiety at  $\lambda = 360\text{ nm}$ . The photoisomerization experiments were carried out with the same sample concentrations for all compounds ( $1.0 \times 10^{-5}\text{ mol/L}$ ). The experiments were followed by using UV spectroscopy and  $^1\text{H NMR}$  spectroscopy (Figure 4). The results proved that the photoisomerization time depends on the terminal substitution and different carbon chains linked between the moieties of the molecules although all molecules reached a photostationary phase within 35 s of photoirradiation. For all compounds, with increases in the radiation time, the absorption peak around  $\lambda = 360\text{ nm}$  started to decrease (*trans*-form), while the peak around  $\lambda = 450\text{ nm}$  increased (*cis*-form). After the photoirradiation was stopped, a slow, thermally driven *cis*–*trans* isomerization took place, the speed of which, again, depended on the terminal substitution pattern and carbon chain lengths within the molecules. Here, for some molecules, the thermal *cis*–*trans* conversion was not totally complete, even after 25 h, where all experiments were carried out at room temperature.



**Figure 3.** UV spectra of **1b**: (a) during irradiation at  $\lambda = 350$  nm (photochemical *trans*–*cis* isomerization of the azobenzene moiety), (b) thermal *cis*–*trans* isomerization of the azobenzene moiety.



**Figure 4.** Monitoring by  $^1\text{H}$  NMR spectroscopy the thermal *cis*–*trans* isomerization of a mixture of *cis*–/*trans*–**1c** after photoirradiation of *trans*–**1c**. The azobenzene unit isomerizes, while the cinnamate moiety remains *trans*–configured during the initial photoisomerization process.

#### 4. Conclusions

A number of 4'-alkoxy-4-( $\omega$ -cinnamoylalkoxy)azobenzenes were prepared. It was found that the azobenzene unit and the cinnamate moiety in these molecules absorb at different wavelengths and can be addressed selectively by photoirradiation. The azo-unit was *trans/cis* isomerized photochemically, while the cinnamate moiety remained *trans*-configured. After the irradiation was halted, the compounds *cis/trans* isomerized thermally. The time the molecules reached photochemical equilibrium depended on the terminal substitution pattern and carbon chain lengths within the molecules. Some of the compounds have been found to exhibit narrow mesophases, so their thermotropic behavior needs to be studied in greater detail. It is expected that the molecules can also be used as switchable dopants in liquid crystalline hosts.

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