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# $^1$H NMR and UV–vis spectroscopy of fluorine and chlorine substituted stilbenes: conformational studies

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## Abstract

UV–vis and $^1$H NMR spectroscopic studies supported by molecular mechanics calculations reveal planar structure for the lowest energy conformations of a series of fluorine- and chlorine-substituted *trans*-stilbenes. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords*: Stilbenes; UV–vis spectroscopy; $^1$H NMR; Molecular mechanics

## 1. Introduction

Recently $^1$H NMR and UV–vis spectroscopic studies of a number of chlorine-substituted stilbenes along with molecular mechanics calculations have been shown to be useful tools for conformational studies of both the *trans* and *cis* isomers in solutions [1]. Correlation was found between the planarity of the molecules and the positions of bands and the vibrational structures observed in the UV absorption spectra of the compounds. Proton chemical shifts were found to be affected by through space effects depending on the positions and number of chlorine substituents on the phenyl rings giving indications of molecular structures.

In this paper, we present UV–vis spectroscopic analysis, which along with molecular mechanic calculations, reveal the structure of the lowest energy conformations for the fluorine and chlorine substituted *trans*-stilbenes **2**–**7** (see Scheme 1). Furthermore, results of $^1$H NMR analysis of compounds **5**, **6** and **7**, which support the prediction, are presented.

## 2. Experimental

### 2.1. Chemicals

The compounds were prepared by the Wadsworth–Emmons modification of the Wittig reaction as depicted in Scheme 2. Refluxing the DME solution of an appropriately substituted benzyltriphenylphosphonium salt and a suitable benzaldehyde derivative in the presence of sodium hydride gave the *trans*-stilbenes in good yields. It was essential to use a base without nucleophilic properties in order to prevent the replacement of fluorine by the base in an aromatic substitution reaction [2].

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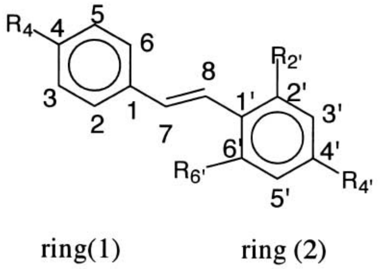


| Com-pound | Halogen positions Ring(1)/ring(2) | $R_4$ | $R_{2'}$ | $R_{4'}$ | $R_{6'}$ |
|---|---|---|---|---|---|
| **1** | - / -- | H | H | H | H |
| **2** | - / 2´Cl6´F | H | **Cl** | H | **F** |
| **3** | - / 2´F6´F | H | **F** | H | **F** |
| **4** | 4Cl / 2´F6´F | **Cl** | **F** | H | **F** |
| **5** | - / -4´F | H | H | **F** | H |
| **6** | 4Cl / -4´F | **Cl** | H | **F** | H |
| **7** | 4F / -4´F | **F** | H | **F** | H |

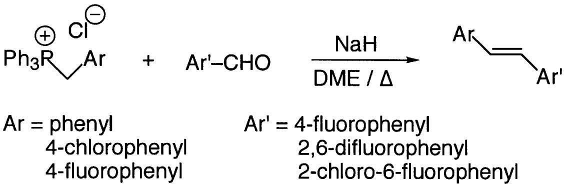
Scheme 1.

### 2.2. UV–vis spectra

UV–vis absorption spectra were measured for all compounds dissolved in *n*-hexane using Varian CARY 100 Bio spectrometer.

### 2.3. $^1$H NMR

Spectra were run on a Bruker AC 250 MHz spectrometer for all compounds dissolved in $CDCl_3$. Chemical shifts were found relative to TMS. These were derived by spectra simulations using the software package gNMR from Cherwell Scientific.



Scheme 2.

## 3. Results and interpretations

### 3.1. Molecular mechanics calculations

Molecular mechanics calculations were performed on a Macintosh computer using the MM3 software package in conjunction with MacMimic from Instar Software. Bond distances and angles were determined for the minimum energy conformations of all the *trans* isomers of compounds **2**–**7** and both the *trans* and *cis* isomers of compound **1**. Minimum energy values were obtained for the compounds as a function of the two dihedral angles, $\theta(1)$ ($C_6$–$C_1$–$C_7$–$C_8$) and $\theta(2)$ ($C_7$–$C_8$–$C_{1'}$–$C_{6'}$) (see Scheme 1) to obtain potential energy surfaces. Thus all the *trans* isomers for compounds **1** and **3**–**7** *were predicted to be planar*. The lowest energy conformation of compound **2** was found to have *near to planar configuration* with F in position $6'$ and Cl in position $2'$, with reference to Scheme 1. The *cis* isomer of compound **1** is found to be nonplanar with dihedral angles about 39°. The predictions for the unsubstituted stilbenes agree with experimental observations [3,4].

Table 1
$^1$H NMR chemical shifts for the *trans* isomers of compounds **1**, **5** and **7**

| Compounds | F positions ring (1)/ring (2) | $\delta(H_{2,6})/\delta(H_{2'6'})$ ppm | $\delta(H_{3,5})/\delta(H_{3'5'})$ ppm | $\delta(H_4)/\delta(H_{4'})$ ppm | $\delta(H_7)$ ppm | $\delta(H_8)$ ppm |
|---|---|---|---|---|---|---|
| **1**[a,b] | –/– | 7.55 | 7.39 | 7.26 | 7.14 | 7.14 |
| **5** | –/4′F | 7.53/7.50 | 7.36/7.39 | 7.30/– | 7.09 | 7.05 |
| **6** | 4Cl/4′F | 7.42/7.47 | 7.33/7.06 | –/– | 7.03 | 6.96 |
| **7**[b] | 4F/4′F | 7.46 | 7.06 | – | 6.98 | 6.98 |

[a] From Ref. [1].

[b] $\delta(H_i) = \delta(H_{i'})$; $i = 2$–6 for the symmetric compounds **1** and **7.**

### 3.2. UV–vis spectroscopy

The UV absorption spectra of the *trans* isomers of compounds **1** and **2** as well as the *cis* isomer of **1** are seen in Fig. 1. The 250–350 nm spectra are believed to be due to a $\pi \rightarrow \pi^*$ transition largely localised in the region of the olefinic double bond [5,6]. The spectra of the compounds **3**–**7** resemble those of the *trans* isomers of compunds **1** and **2**, showing vibrational structure on the long wavelength side of a broad peak with maximum between about 290–300 nm. This has been shown to be characteristic for a planar structure, while nonplanar isomers (both *cis* and *trans* isomers) show structureless broad peaks at shorter wavelength analogous to that found for *cis*-**1**. Hence the UV spectra observations for the *trans* isomers of compounds **2**–**7** support the above-mentioned predictions *of planar molecular structures*.

### 3.3. $^1H$ NMR chemical shifts

$^1$H NMR chemical shifts for the *trans* isomers of compounds **1** and **5**–**7** are listed in Table 1. The ethylene protons ($H_7$ and $H_8$) are found to undergo upfield shifts, gradually increasing with the number of F (and Cl) substituents in positions 4 (4′) as $\mathbf{1} < \mathbf{5}$ $(< \mathbf{6}) < \mathbf{7}$, analogous to that which was found for chlorine substituted *trans*-stilbens [1]. This we associate with the effect of decreasing ring current on the phenyl rings as the electron withdrawing substituents are added to the rings, *to be expected for flat molecular geometry*. Furthermore the ring

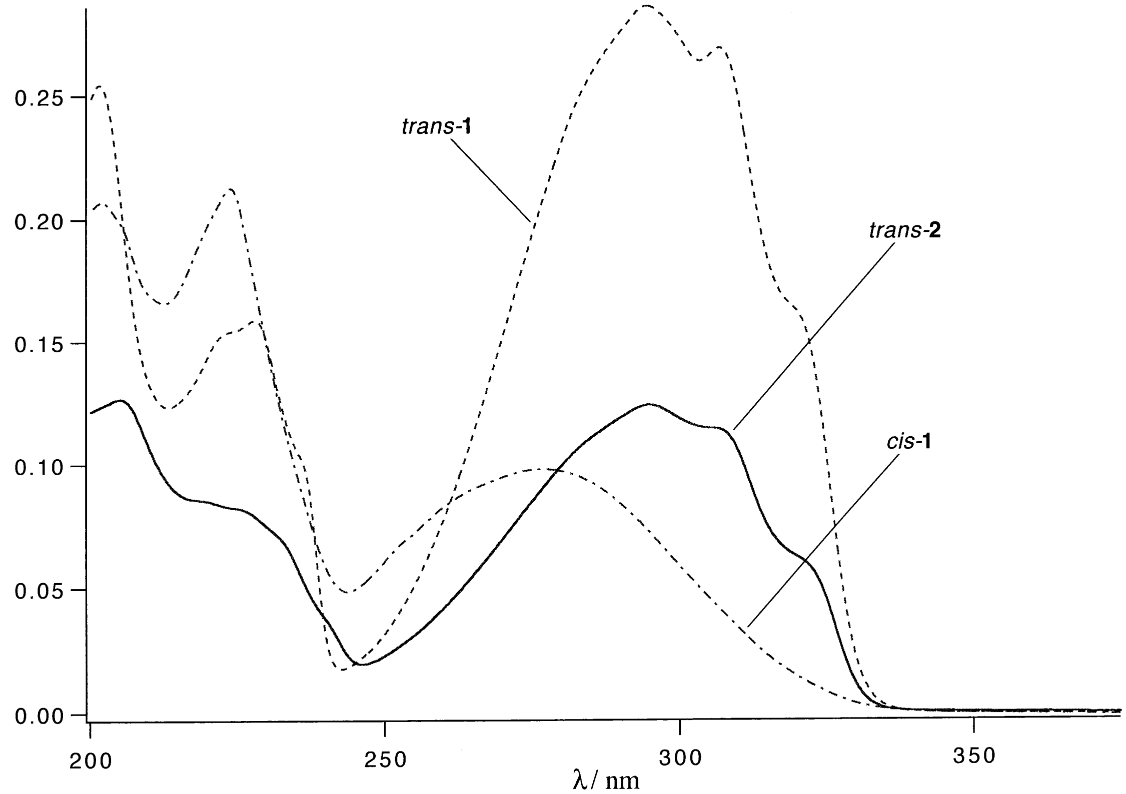


Fig. 1. UV absorption spectra of compounds *trans*-**1**, *cis*-**1** and *trans*-**2** dissolved in *n*-hexane. Vibrational structure, appearing as broad peaks or shoulders in the spectral region 250–350 nm is found for compounds with planar geometry (such as *trans*-**1** and *trans*-**2**) only. Peak maxima in this spectral region shift to shorter wavelength as the molecular structure changes from planar to nonplanar (*cis*-**1**). Spectra are for $1 \times 10^{-5}$ M solutions in 1 cm wide cuvettes.

protons $H_2/H_6$ ($H_{2'}/H_{6'}$) and $H_3/H_5$ ($H_{3'}/H_{5'}$) are also found to undergo small but significant upfield shifts with increasing number of F (and Cl) substituents, which also could be explained as being due to decreasing ring current effects.

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