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Journal of Photochemistry and Photobiology A: Chemistry 115 (1998) 57–61

Journal of Photochemistry and Photobiology A:Chemistry

# Photochemistry of substituted methyl-$\alpha$-arylcinnamates: *ortho*- and *para*-substitution

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Received 27 October 1997; received in revised form 9 February 1998; accepted 10 February 1998

## Abstract

The 308 nm laser photochemistry of a series of substituted methyl-$\alpha$-arylcinnamates has been studied in deoxygenated hexane and acetonitrile. Methyl-$\alpha$-phenylcinnamate (**1a**) and derivatives that are *p*-substituted with electron withdrawing (chloro, **1b**) or electron donating (methoxy, **1c**) groups exhibited very similar photochemistry and spectroscopic properties, with the photostationary state (pss) composition ([*E*]/[*Z*]) being, on the average, 2.8 for these substances. By contrast the pss value for the *o,o*-dichloro substituted arylcinnamate (**1d**) was found to be only 0.5. This difference is discussed in terms of possible influences of the *o,o*-dichloro substituents on the excited state potential energy surface for arylcinnamate photoisomerization.

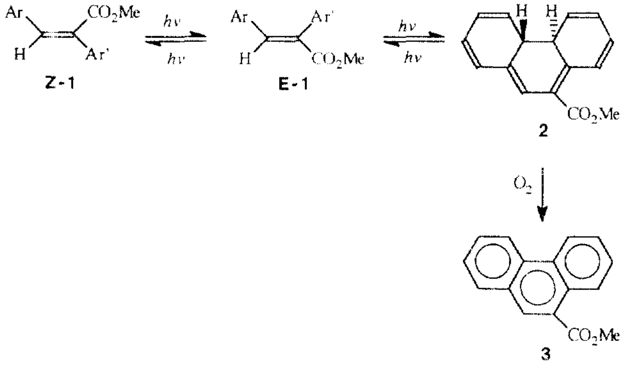
*Keywords:* Photochemistry; Methyl-$\alpha$-arylcinnamates; *Ortho*- and *para*-substitution

## 1. Introduction

Photoisomerization of ethylenic molecules has been the subject of intense study for decades. This interest arises from the potential to obtain detailed understanding of the events resulting in relaxation in chemical systems after electronic excitation by light [1–3]. Olefinic photoisomerizations also play a central role in biological phototropic systems such as vision and photomorphism in plants [4,5]. Photoisomerizations are relatively easy to study and are chemically simple.

The prototype olefin photoisomerization is the *trans*- to *cis*-stilbene phototransformation. A great deal of effort has been placed on studying all aspects of this reaction and a fairly detailed picture has developed [1,2,6–12]. One of the major achievements has been the detailed elucidation of the potential energy surfaces involved in the isomerization.

Methyl-$\alpha$-phenylcinnamate, **1a**, is a stilbene derivative which undergoes E/Z photoisomerization from the excited singlet state as well as a ring closure reaction to form the 4a,4b-dihydrophenanthrene derivative (**2**) [13,14]. In the presence of oxidizing agents, this species converts to methyl-9-phenanthroate (**3**) [13,14]. These processes are summarized in Scheme 1. Cinnamates are of current research interest because of their use for the design of photoactive polymers, molecular assemblies, supramolecular devices and UV filters [15].



Scheme 1. Photochemical processes open to methyl-$\alpha$-arylcinnamate in hexane.

We report here our most recent study of substituted methyl-$\alpha$-arylcinnamate photochemistry. The series investigated includes compounds *para*-substituted with an electron withdrawing, electron donating or electroneutral group on the $\alpha$-phenyl ring as well as a compound that is *o,o*-dichloro substituted on the $\beta$-phenyl ring. The cinnamate derivatives used in this work are depicted in Scheme 2. While ring substitution in stilbene derivatives is not normally recognized as

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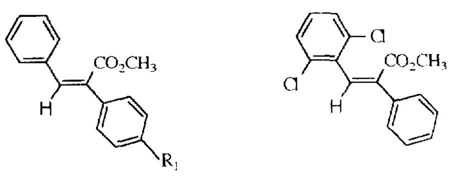
*PII* S1010-6030(98)00243-3



$R_1$ = H, **1a**
$R_1$ = Cl, **1b**
$R_1$ = $OCH_3$, **1c**

**1d**

Scheme 2. Structures of the arylcinnamates examined, Z-isomers only.

leading to major changes in photochemistry [1,16,17], we have observed a significant effect of *o,o*-dichloro substitution on the *β*-phenyl ring.

## 2. Experimental

Methyl-*α*-phenylcinnamate isomers (***E*-1a** and **Z-1a**) and their derivatives were prepared via the Horner–Wadsworth–Emmons modification of the Wittig reaction [13,18]. Individual isomers were found to be pure ( > 99%) by HPLC and GC.

Methyl-9-phenanthroate (**3**) was prepared by literature procedures [19]. Solvents were of the highest quality commercially available (spectral or HPLC grade) and were used as received. Inorganic salts (Janssen, BDH, Merck) were used as received. Nitrogen was of ultra-high purity grade.

Photostationary states were prepared by photolysing $1\times10^{-4}$ M samples of the cinnamates in degassed hexane with pulses (308 nm, ca. 10 ns, ≤40 mJ/pulse) from a Lumonics 510 excimer laser operating with a XeCl mixture. The photostationary state compositions were obtained via analytical HPLC using an LDC Analytical Consta Metric 3200 HPLC system operating with a 10-cm column. The mobile phase was 1% ethylacetate in *n*-hexane. Detection was based on absorbance at 280 nm. HPLC response was calibrated against authentic samples.

Quantum yields for isomerization and phenanthrene formation were determined by ferrioxalate actinometry using the arrangement recommended by Murov et al. [20] and Bunce [21] for laser excitation.

Fluorescence spectra of $1\times10^{-4}$ M esters in hexane or methylcyclohexane were recorded at room temperature with a Spex FluoroMax Spectrofluorometer (Instruments SA). Excitation was at 270 nm and the band width was typically 2 nm. The emission spectra were uncorrected. Absorption spectra were recorded with a Shimadzu UV–Visible Absorption Spectrometer.

The laser flash photolysis apparatus used for one- and two-laser experiments has been described in detail elsewhere [22,23]. In the one-laser experiment, samples were irradiated by the UV pulses of a Lumonics EX 510 excimer laser (308 nm, 10 ns, ≤40 mJ/pulse). In the two-laser experiment, the UV laser was followed after a short delay by the pulse from a Candela SLL 250 flashlamp-pumped dye laser using a Coumarin 480 dye (488 nm, 350 ns, ≤150 mJ). Ester samples, ca. $1\times10^{-4}$ M in acetonitrile, were allowed to flow continuously through a specially constructed $7\times7$ $mm^2$ quartz cell, ensuring that a fresh volume of sample was irradiated by each laser pulse (or pair of pulses in the two-laser experiments). Unless otherwise indicated all samples were deoxygenated before irradiation by bubbling a stream of nitrogen through the sample for 20 min. For flowing samples, nitrogen was continuously bubbled through the sample reservoir.

Molecular mechanics calculations for the ground states of the cinnamates were performed in a Macintosh environment using the MM2(91) software package in conjunction with MacMimic from Instar Software.

## 3. Results

Table 1 summarizes photostationary state compositions and isomerization quantum yields for **1a** and three substituted derivatives. The same pss composition was obtained starting from the *E*- or the *Z*-isomer. For **1a** and its *p*-substituted derivatives (**1b**, **1c**) the photostationary state (pss) composition was found to be rich in the *E*-isomer as has been reported previously for related compounds [13,14]. The behavior of the *o,o*-dichlorocinnamate, **1d**, was in marked contrast to **1a** and its *para* derivatives in that the pss contained much more *Z*- than *E*-isomer.

Table 2 summarizes ground state absorption data for the cinnamates. In each case, the bands were broad and featureless and there is little difference between the *E*- and *Z*-isomers. In terms of transition energies, **1a** and its *para* derivatives were similar to each other and to other arylcinnamates that have been examined [13]. That the absorption of both *E*- and *Z*-arylcinnamates generally resembles that of *cis*-stilbene [3,13] has been attributed to larger angles of

Table 1
Photostationary state composition and quantum yields for the cinnamate esters following 308 nm irradiation in deoxygenated hexane

| Ester | pss [a] | $\phi_{EZ}$ [b] | $\phi_{ZE}$ [b] |
|---|---|---|---|
| **1a** | 2.5 | 0.2 | 0.5 |
| **1b** | 2.8 | 0.1 | 0.2 |
| **1c** | 3.1 | 0.2 | 0.6 |
| **1d** | 0.5 | 0.05 | 0.01 |

[a] Pss is the ratio [***E*-1**]/[**Z-1**] determined by HPLC.
[b] Quantum yields for *E* to *Z* and *Z* to *E* isomerization, ± 10%.

Table 2
Ground state absorption maxima for the *E*-cinnamate esters

| Ester | $\lambda_{max}$ (nm) | Ester | $\lambda_{max}$ (nm) |
|---|---|---|---|
| ***E*-1a** | 282 | ***Z*-1a** | 283 |
| ***E*-1b** | 284 | ***Z*-1b** | 283 |
| ***E*-1c** | 275 (320) | ***Z*-1c** | 275 (320) |
| ***E*-1d** | 265 | ***Z*-1d** | 263 |

( ) = shoulder.

twist between the aryl groups and the plane of the double bond in the arylcinnamates as compared to stilbene, even when the aryl rings are in a *trans* conformation [13]. The degree of non-planarity will be large in both the *E*- and *Z*-arylcinnamates as large groups are present on both sides of the double bond in these systems. In this sense, both *E*- and *Z*-cinnamates resemble *cis*-stilbene (relatively large phenyl ring twist angle) rather than *trans*-stilbene (smaller phenyl ring twist angle). These trends were confirmed by the molecular modelling estimates of the aryl group twist angles presented in Table 3.

The band maximum of **1d** was significantly blue shifted relative to the three other compounds examined here and in fact lay in a range similar to that observed for alkylcinnamates [24]. The results presented in Table 3 suggest that this may be due to the extreme non-planarity of **1d** in the ground state resulting in minimal resonance interaction of the 2,6-disubstituted ring with the rest of the molecule's $\pi$-system.

Fig. 1 shows a series of fluorescence spectra measured for $1 \times 10^{-4}$ M *E*-**1a** in air saturated hexane at room temperature. The spectra were measured without sample flow. They represent different periods of time that the sample was in the cell holder of the fluorometer and subject to excitation at 270 nm. The first spectrum ('zero' time) represents, at most, 1 min of 270 nm exposure. As the exposure time increased, the intensities of the bands at 360, 378 and 400 nm also increased. We assign the fluorescence observed between 350 and 450 nm to emission from the ring closure oxidation product, methyl-9-phenanthroate (**3a**, Scheme 1). This assignment is based on measurement of the fluorescence spectrum of a genuine sample of **3a** which proved to have features identical to those shown in Fig. 1. Similar phenanthrene-like fluorescence spectra were obtained for all four *E*-cinnamates upon photolysis in the cell holder of the fluorometer. In each case, we attribute the observed fluorescence to formation of the corresponding fully oxidized phenanthroate derivative.

Room temperature fluorescence was also recorded under non-flow conditions for the *Z*-isomers. Essentially, the same behavior was observed for the *Z*-isomers as for the *E*-isomers. That is, formation of progressively increasing amounts of the corresponding phenanthroate **3** were observed. Presumably, this occurs via *Z* to *E* photoisomerization within the fluorimeter. The very weak fluorescence observed at short times (zero time) after the samples are exposed to the light from the fluorometer, and the fact that it is in the same spectral region as the fluorescence of the corresponding phenanthroates indicates that the cinnamates have a very small fluorescence quantum yield, i.e., below the sensitivity threshold of our fluorometer. This is in accord with the fluorescence quantum yield for *cis*-stilbene of ca. 0.0001 reported by Saltiel et al. [25]. The fact that the *Z*-cinnamate also has a negligible fluorescence yield contrasts with *trans*-stilbene for which $\phi_f$ is ca. 0.04 [1]. Again this can be explained by the fact that steric interaction between the large groups on the double bond reduces resonance within the molecule with the probable result that the small (ca. 4 kcal/mol [1–3]) stabilization of *trans*-stilbene on the excited state surface is lost in the *Z*-cinnamate.

Table 3

Out-of-plane aryl ring twisting angles for various stilbene derivatives. $\alpha^0$ and $\beta^0$ refer to the angles of the ring on the ester-bearing carbon and the hydrogen-bearing carbon, respectively [a]

| | *E*-isomer | *E*-isomer | *Z*-isomer | *Z*-isomer |
|---|---|---|---|---|
| | $\alpha^0$ | $\beta^0$ | $\alpha^0$ | $\beta^0$ |
| Stilbene | 30–50 [b] | – | 'nearly planar' [c] | – |
| **1a** | 44 | 39 | 35 | 47 |
| **1b** | 44 | 39 | 34 | 45 |
| **1c** | 44 | 37 | 36 | 45 |
| **1d** | 43 | 62 | 37 | 72 |

[a] Results of molecular mechanics calculations, except where noted.

[b] Experimental value for *cis*-stilbene rings quoted in Ref. [1].

[c] Experimental value for *trans*-stilbene rings quoted in Ref. [1].

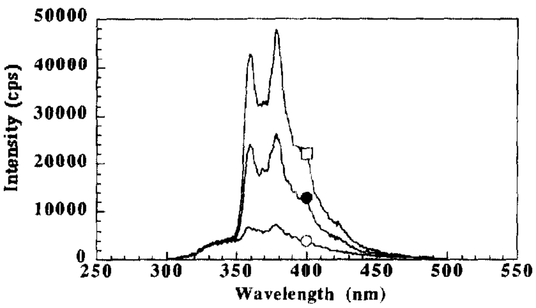


Fig. 1. Fluorescence spectra of $1 \times 10^{-4}$ M *E*-**1a** measured in deoxygenated hexane. (○) 'Zero' irradiation time (ca. 1 min exposed to fluorometer source); (○) 20 min irradiation time; (□) 40 min irradiation time. Excitation at 270 nm.

Fig. 2 shows the transient absorption spectrum obtained when $1 \times 10^{-4}$ M *E*-**1a** was irradiated with 308 nm excimer

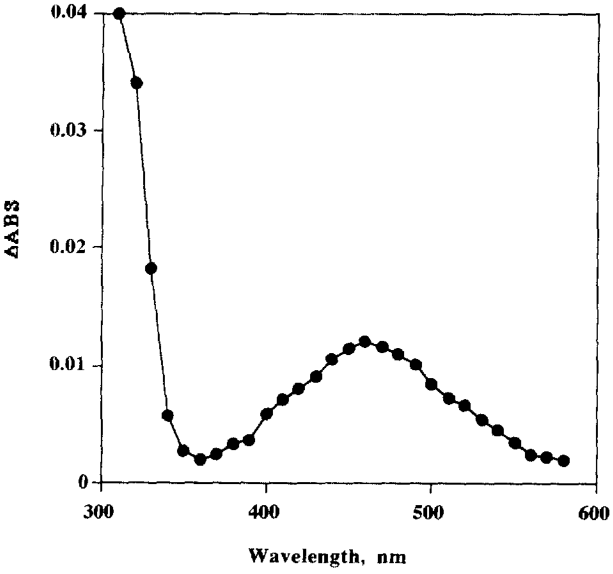


Fig. 2. Transient absorption spectrum of **2a** recorded 210 μs after 308 nm laser photolysis of a flowing, deoxygenated $1 \times 10^{-4}$ M solution of **1a** in acetonitrile.

laser pulses in flowing, deoxygenated acetonitrile. The UV absorption which appears as a sharply rising shoulder and the weaker visible absorption centered near 460 nm are characteristic of the absorption of the 4a,4b-dihydrophenanthrene (DHP, **2**) intermediates formed upon initial ring closure of stilbene derivatives [26]. For example, the DHP of stilbene itself exhibited bands at 450 (band I), 310 and 297 (band II), and 237 nm (band III) [26,27]. We were only able to observe band I and the shoulder of band II in our system because of increasing absorption by the **1a** ground state below 300 nm. The transient absorption was thus distorted by depletion of the ground state at these wavelengths.

The transient shown in Fig. 2 was found to be very long lived, showing no decay over a period of 2 ms, the longest measurable time scale of our instrument. This is also consistent with the lifetime reported for **2a** which was several minutes in deoxygenated hexane [14]. It is safe to conclude, then, that the transient absorption in Fig. 2 is that of dihydrophenanthrene **2a**.

Additional evidence for this assignment was provided by the results of two-laser experiments. In these experiments, 308 nm irradiation of $1\times10^{-4}$ M ***E*-1a** in flowing hexane resulted in formation of **2a**. Subsequent irradiation of the DHP with a pulse at 488 nm from the dye laser firing a few μs after the 308 nm pulse, resulted in complete bleaching of the transient absorption. As there was virtually no conversion of the ground state ($<10\%$) as judged by ground state absorption measurements, we can conclude that the second pulse is causing a photochemical reversion of **2a** to ***E*-1a**, which is itself a known process, Scheme 1 [26].

Similar spectra and lifetimes were observed for **1b** and **1c** in flowing, deoxygenated acetonitrile. The only difference between these two transients and **1a** was that band I of **1c** was relatively weak compared to that of **1a** and **1b**. The transients observed for **1b** and **1c** may thus also be attributed to their corresponding DHPs.

The transient spectrum (Fig. 3) obtained when **1d** was photolyzed with 308 nm laser pulses in flowing, deoxygenated acetonitrile was different than those observed for the other three cinnamates. Bands I and II were now both clearly observed as a result of a red shift. This change in the spectral properties corresponds to an earlier report of the DHP spectrum for 2,2′,4,4′,6,6′-hexamethyl-stilbene which absorbs at 475 (band I), 320 and 310 (band II), and 245 nm (band III), [27,28].

## 4. Discussion

The observation of *E*-rich pss compositions for cinnamates **1a–c** makes them typical of arylcinnamates (Table 1) [13]. This is in contrast to pss values observed for alkylcinnamates which are smaller by about a factor of 3 when irradiation takes place at similar wavelengths [24]. It has been proposed [13] that this difference is due to the fact that the arylcinnamates have an additional reaction channel open to them, namely ring closure to form dihydrophenanthrenes (DHPs), which reduces the amount of excited *E*-isomer available to undergo isomerization. In turn this reduces the amount of *Z* remaining in the pss. While our transient results indicate that ring closure to the DHP form occurs for all the cinnamates studied, there is a significant reduction in the amount of *E*-isomer relative to *Z*-isomer in the pss of **1d**, i.e., the compound with the *o,o*-dichloro substitution of the β-ring. In fact nearly all the properties of **1d** examined in this study differ markedly from those of the *p*-substituted analogs, **1a–c**.

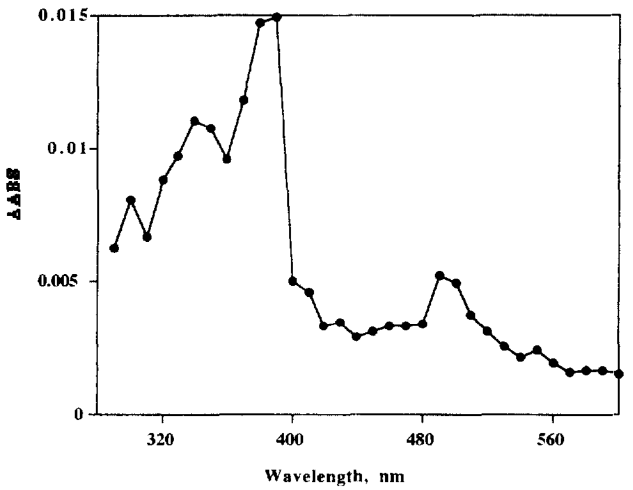


Fig. 3. Transient absorption spectrum of **2d** recorded 210 μs after 308 nm laser photolysis of a flowing, deoxygenated $1\times10^{-4}$ M solution of **1d** in acetonitrile.

Pss composition can be calculated according to Eq. (1) [3]

$$\left(\frac{[E]}{[Z]}\right)_{\mathrm{pss}}=\left(\frac{\varepsilon_Z}{\varepsilon_E}\right)\times\left(\frac{\phi_{ZE}}{\phi_{EZ}}\right) \qquad (1)$$

Thus, in principle, the apparent difference in $[E]/[Z]$ ratio for **1d** relative to **1a–c** could have its origin in different extinction coefficients of the **1d** isomers and/or a smaller *Z*- to *E*-isomerization quantum yield for **1d** than for **1a–c**. In other words, the effect is spectroscopic and/or photochemical in nature. However, the close similarity of the absorption spectra of all the *E*- and *Z*-arylcinnamates (Table 2) and similar *Z*/*E* extinction coefficient ratios ($\varepsilon_Z/\varepsilon_E$: **1a**, 1.6 [13]; **1b**, 1.7 [13]; **1c**, 1.1; **1d**, 2.0) allow the conclusion that in the case of **1d** it is clearly a photochemical effect, i.e., the ratio of quantum yields, that results in the observation of a *Z*-rich pss. Furthermore, since the quantum yield for the *E* to *Z* process in **1d** is comparable to those observed for the *para*-substituted esters **1a–c**, it is the quantum yield for the *Z*-to-*E* conversion that is smaller—by as much as a factor of 60—than the values observed for the other three cinnamates. Thus, the small value of $\phi_{ZE}$ is primarily responsible for the enrichment of *Z* in the pss.

The source of the low $\phi_{ZE}$ value is apparently not electronic in nature as electron donating or withdrawing substitution at other locations (**1a–1c**) has no influence on the arylcinnamate photochemistry. Recent work [6,12] on potential energy surfaces for stilbene photoisomerization has shown that the details of the decay processes for the Franck–Condon excited *cis*- and *trans*-stilbene depend strongly on the extent of interaction between the two phenyl rings as well as on the twist angle about the (former) double bond following excitation. These two properties are in fact reaction coordinates for relaxation from the excited surface to the ground state surface. The decay routes open to excited *cis*-stilbene are found to be combinations of twist angle and ring separation. Any given relaxation path may be dominated by one or the other factor or an admixture of both. By contrast, the behavior of excited *trans*-stilbene is dominated by movement along the 'bond twist' coordinate as the ring separation is fairly large and the interaction between rings fairly weak in this case. In the context of the arylcinnamates one might expect group–group interactions to play a role even for the *Z*-isomers (which correspond to *trans*-stilbene) because of the presence of the ester group. This will be even more relevant in the case of **1d** where the sterically large *o,o*-dichloro substitution will strengthen ring–ring (for ***E*-1d**) and ring–ester (for **Z-1d**) interactions. One may thus conclude that the decay paths open to the Franck–Condon excited states of ***E*-1d** and **Z-1d** can be very different from those proposed for the corresponding excited stilbenes and also from those available to the less sterically constrained **1a–1c**. It seems likely, then, that the difference in pss value for **1d** vs. **1a–c** can be traced to differences in the nature of the group–group reaction coordinate on the corresponding excited state surfaces.

## 5. Conclusion

In summary, we have observed that *o,o*-dichloro substitution of methyl $\alpha$-phenylcinnamate causes a dramatic change in the composition of the pss from *E*-isomer-rich to *Z*-isomer-rich. This can be traced to variations in the value of the *Z* to *E* photoisomerization quantum yield which probably arise due to differences in the degree of interaction between large groups attached to the $\alpha$- and $\beta$-carbons of the double bond on the excited state reaction surface. In order to gain more insight into this issue we are currently undertaking a study involving a series of *o,o*-disubstituted arylcinnamates in which the steric size and electronic character of the substituents is varied.

## Acknowledgements

The authors gratefully acknowledge the financial support of The University of Iceland Research Fund. Partial funding of the purchase of the fluorescence instrument from The Equipment Purchase Fund of the University of Iceland and The Icelandic Research Council (Vísindasjódur and Byggingasjódur) is also greatly appreciated.

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